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*Supporting Materials for:*

# Organobase Catalyzed Straightforward Synthesis of Phosphinyl Functionalized 2H-Pyran Cores from Allenylphosphine Oxides and 1,3-Diones

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## 1. General Methods

Solvents and reagents were of reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follows: THF, 1,4-dioxane and toluene were dried by distillation from sodium and benzophenone; DCE, DMSO were redistilled over $CaH_2$. All reactions were carried out in oven dried glassware unless otherwise specified. Column chromatography was performed using silica gel (300-400 mesh). $^{1}H$ NMR, $^{13}C$ NMR and $^{31}P$ NMR spectra were recorded in $CDCl_3$ operating at 400, 100 and 162 MHz in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad. High resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument using EI (70 eV) or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

## 2. General Procedure for the Synthesis of *2H*-Pyran Derivatives

To a 15 mL sealed reaction tube, allenylphosphine oxide (**1a**, 120 mg, 0.3 mmol), 5,5-dimethylcyclohexane-1,3-dione (**2a**, 84 mg, 0.6 mmol) and DMAP (7 mg, 0.06 mmol, for condition A) or DBU (9 mg, 0.06 mmol, for condition B) were dissolved in 3 mL 1,4-dioxane. The reaction mixture was then heated to reflux for 3 h until the complete consuming of **1a** as monitored by TLC. After all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloro-methane) to afford product **3aa** as a white solid.

## 3. General Procedure for the Synthesis of Intermediate

To a 15 mL sealed reaction tube, allenylphosphine oxide (**1a**, 120 mg, 0.3 mmol), ethyl 3-oxobutanoate (**2e**, 78 mg, 0.6 mmol) and DMAP (7 mg, 0.06 mmol) were dissolved in 3 mL 1,4-dioxane. The reaction mixture was then heated to reflux for 3 h until the complete consuming of **1a** as monitored by TLC. After all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloro-methane) to afford product **3ae'** as a yellow liquid.

## 4. X-Ray Crystallography Data of 3aa

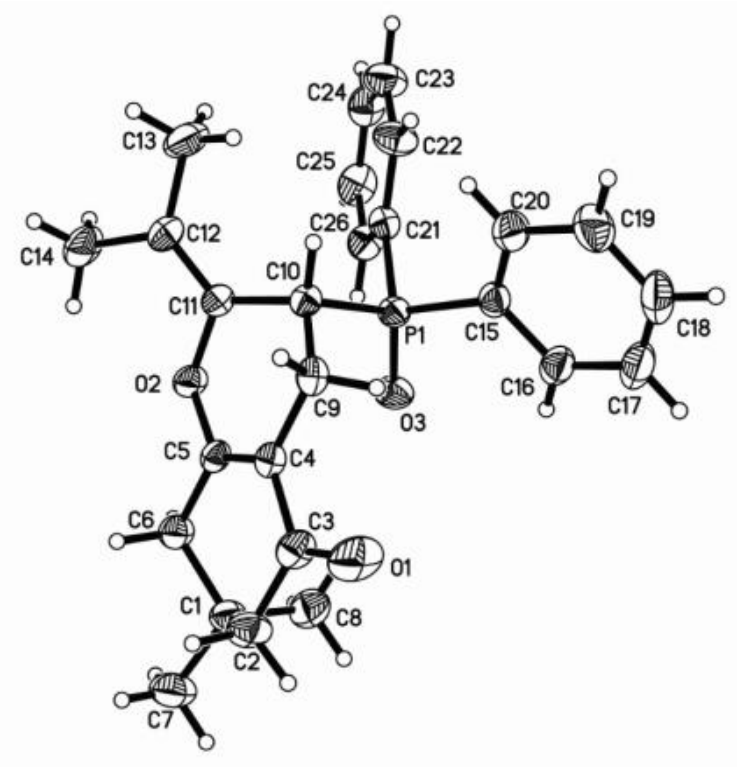


Table 1. Crystal data and structure refinement for **3aa**.

| | | |
|---|---|---|
| Identification code | 3aa | |
| Empirical formula | C26 H29 O3 P | |
| Formula weight | 420.46 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | a = 9.6804(14) Å | α= 90 °. |
| | b = 24.788(4) Å | β= 109.906(4) °. |
| | c = 10.4180(16) Å | γ = 90 °. |
| Volume | 2350.5(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.188 $Mg/m^3$ | |
| Absorption coefficient | 0.140 $mm^{-1}$ | |
| F(000) | 896 | |
| Crystal size | 0.210 x 0.180 x 0.150 $mm^3$ | |
| Theta range for data collection | 2.384 to 27.513 °. | |
| Index ranges | -12<=h<=12, -32<=k<=32, -13<=l<=13 | |
| Reflections collected | 32944 | |
| Independent reflections | 5386 [R(int) = 0.0399] | |

| | |
|---|---|
| Completeness to theta = 25.242 ° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5386 / 0 / 275 |
| Goodness-of-fit on $F^2$ | 1.027 |
| Final R indices [I>2sigma(I)] | R1 = 0.0490, wR2 = 0.1280 |
| R indices (all data) | R1 = 0.0789, wR2 = 0.1413 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.242 and -0.242 e.$Å^{-3}$ |

Table 2. Bond lengths [Å] and angles [ °] for **3aa**.

| | |
|---|---|
| C(1)-C(8) | 1.524(3) |
| C(1)-C(2) | 1.530(3) |
| C(1)-C(7) | 1.533(3) |
| C(1)-C(6) | 1.533(3) |
| C(2)-C(3) | 1.508(3) |
| C(2)-H(2A) | 0.9700 |
| C(2)-H(2B) | 0.9700 |
| C(3)-O(1) | 1.229(2) |
| C(3)-C(4) | 1.454(2) |
| C(4)-C(5) | 1.340(2) |
| C(4)-C(9) | 1.496(2) |
| C(5)-O(2) | 1.3621(18) |
| C(5)-C(6) | 1.488(2) |
| C(6)-H(6A) | 0.9700 |
| C(6)-H(6B) | 0.9700 |
| C(7)-H(7A) | 0.9600 |
| C(7)-H(7B) | 0.9600 |
| C(7)-H(7C) | 0.9600 |
| C(8)-H(8A) | 0.9600 |
| C(8)-H(8B) | 0.9600 |
| C(8)-H(8C) | 0.9600 |
| C(9)-C(10) | 1.539(2) |
| C(9)-H(9A) | 0.9700 |
| C(9)-H(9B) | 0.9700 |
| C(10)-C(11) | 1.503(2) |
| C(10)-P(1) | 1.8328(16) |

| | |
|---|---|
| C(10)-H(10) | 0.9800 |
| C(11)-C(12) | 1.328(2) |
| C(11)-O(2) | 1.404(2) |
| C(12)-C(13) | 1.501(3) |
| C(12)-C(14) | 1.513(3) |
| C(13)-H(13A) | 0.9600 |
| C(13)-H(13B) | 0.9600 |
| C(13)-H(13C) | 0.9600 |
| C(14)-H(14A) | 0.9600 |
| C(14)-H(14B) | 0.9600 |
| C(14)-H(14C) | 0.9600 |
| C(15)-C(20) | 1.383(3) |
| C(15)-C(16) | 1.392(3) |
| C(15)-P(1) | 1.8145(18) |
| C(16)-C(17) | 1.382(3) |
| C(16)-H(16) | 0.9300 |
| C(17)-C(18) | 1.358(4) |
| C(17)-H(17) | 0.9300 |
| C(18)-C(19) | 1.375(4) |
| C(18)-H(18) | 0.9300 |
| C(19)-C(20) | 1.393(3) |
| C(19)-H(19) | 0.9300 |
| C(20)-H(20) | 0.9300 |
| C(21)-C(22) | 1.385(3) |
| C(21)-C(26) | 1.389(3) |
| C(21)-P(1) | 1.8109(18) |
| C(22)-C(23) | 1.379(3) |
| C(22)-H(22) | 0.9300 |
| C(23)-C(24) | 1.376(3) |
| C(23)-H(23) | 0.9300 |
| C(24)-C(25) | 1.363(3) |
| C(24)-H(24) | 0.9300 |
| C(25)-C(26) | 1.376(3) |
| C(25)-H(25) | 0.9300 |
| C(26)-H(26) | 0.9300 |
| O(3)-P(1) | 1.4812(13) |

| | |
|---|---|
| C(8)-C(1)-C(2) | 110.67(18) |

| | |
|---|---|
| C(8)-C(1)-C(7) | 109.75(18) |
| C(2)-C(1)-C(7) | 110.97(17) |
| C(8)-C(1)-C(6) | 109.79(16) |
| C(2)-C(1)-C(6) | 107.05(16) |
| C(7)-C(1)-C(6) | 108.54(16) |
| C(3)-C(2)-C(1) | 114.20(15) |
| C(3)-C(2)-H(2A) | 108.7 |
| C(1)-C(2)-H(2A) | 108.7 |
| C(3)-C(2)-H(2B) | 108.7 |
| C(1)-C(2)-H(2B) | 108.7 |
| H(2A)-C(2)-H(2B) | 107.6 |
| O(1)-C(3)-C(4) | 120.62(18) |
| O(1)-C(3)-C(2) | 121.21(17) |
| C(4)-C(3)-C(2) | 118.15(16) |
| C(5)-C(4)-C(3) | 118.45(16) |
| C(5)-C(4)-C(9) | 122.03(14) |
| C(3)-C(4)-C(9) | 119.40(15) |
| C(4)-C(5)-O(2) | 123.58(15) |
| C(4)-C(5)-C(6) | 125.52(15) |
| O(2)-C(5)-C(6) | 110.89(13) |
| C(5)-C(6)-C(1) | 113.06(15) |
| C(5)-C(6)-H(6A) | 109.0 |
| C(1)-C(6)-H(6A) | 109.0 |
| C(5)-C(6)-H(6B) | 109.0 |
| C(1)-C(6)-H(6B) | 109.0 |
| H(6A)-C(6)-H(6B) | 107.8 |
| C(1)-C(7)-H(7A) | 109.5 |
| C(1)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(1)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| C(1)-C(8)-H(8A) | 109.5 |
| C(1)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(1)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |

| | |
|---|---|
| C(4)-C(9)-C(10) | 110.35(13) |
| C(4)-C(9)-H(9A) | 109.6 |
| C(10)-C(9)-H(9A) | 109.6 |
| C(4)-C(9)-H(9B) | 109.6 |
| C(10)-C(9)-H(9B) | 109.6 |
| H(9A)-C(9)-H(9B) | 108.1 |
| C(11)-C(10)-C(9) | 111.36(13) |
| C(11)-C(10)-P(1) | 112.21(11) |
| C(9)-C(10)-P(1) | 109.85(11) |
| C(11)-C(10)-H(10) | 107.7 |
| C(9)-C(10)-H(10) | 107.7 |
| P(1)-C(10)-H(10) | 107.7 |
| C(12)-C(11)-O(2) | 116.13(15) |
| C(12)-C(11)-C(10) | 128.67(16) |
| O(2)-C(11)-C(10) | 115.19(13) |
| C(11)-C(12)-C(13) | 123.03(18) |
| C(11)-C(12)-C(14) | 121.70(18) |
| C(13)-C(12)-C(14) | 115.27(16) |
| C(12)-C(13)-H(13A) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(12)-C(14)-H(14A) | 109.5 |
| C(12)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| C(12)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |
| H(14B)-C(14)-H(14C) | 109.5 |
| C(20)-C(15)-C(16) | 118.74(18) |
| C(20)-C(15)-P(1) | 124.07(14) |
| C(16)-C(15)-P(1) | 117.01(16) |
| C(17)-C(16)-C(15) | 120.5(2) |
| C(17)-C(16)-H(16) | 119.8 |
| C(15)-C(16)-H(16) | 119.8 |
| C(18)-C(17)-C(16) | 120.1(2) |
| C(18)-C(17)-H(17) | 119.9 |

| | |
|---|---|
| C(16)-C(17)-H(17) | 119.9 |
| C(17)-C(18)-C(19) | 120.7(2) |
| C(17)-C(18)-H(18) | 119.6 |
| C(19)-C(18)-H(18) | 119.6 |
| C(18)-C(19)-C(20) | 119.7(2) |
| C(18)-C(19)-H(19) | 120.2 |
| C(20)-C(19)-H(19) | 120.2 |
| C(15)-C(20)-C(19) | 120.2(2) |
| C(15)-C(20)-H(20) | 119.9 |
| C(19)-C(20)-H(20) | 119.9 |
| C(22)-C(21)-C(26) | 117.85(18) |
| C(22)-C(21)-P(1) | 125.34(14) |
| C(26)-C(21)-P(1) | 116.80(14) |
| C(23)-C(22)-C(21) | 120.5(2) |
| C(23)-C(22)-H(22) | 119.7 |
| C(21)-C(22)-H(22) | 119.7 |
| C(24)-C(23)-C(22) | 120.5(2) |
| C(24)-C(23)-H(23) | 119.8 |
| C(22)-C(23)-H(23) | 119.8 |
| C(25)-C(24)-C(23) | 119.8(2) |
| C(25)-C(24)-H(24) | 120.1 |
| C(23)-C(24)-H(24) | 120.1 |
| C(24)-C(25)-C(26) | 120.0(2) |
| C(24)-C(25)-H(25) | 120.0 |
| C(26)-C(25)-H(25) | 120.0 |
| C(25)-C(26)-C(21) | 121.36(19) |
| C(25)-C(26)-H(26) | 119.3 |
| C(21)-C(26)-H(26) | 119.3 |
| C(5)-O(2)-C(11) | 119.30(12) |
| O(3)-P(1)-C(21) | 111.44(8) |
| O(3)-P(1)-C(15) | 111.51(8) |
| C(21)-P(1)-C(15) | 109.08(8) |
| O(3)-P(1)-C(10) | 114.93(8) |
| C(21)-P(1)-C(10) | 106.44(8) |
| C(15)-P(1)-C(10) | 102.94(8) |

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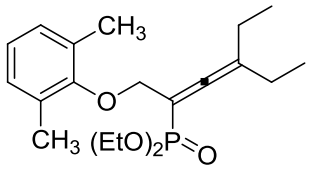
Symmetry transformations used to generate equivalent atoms:

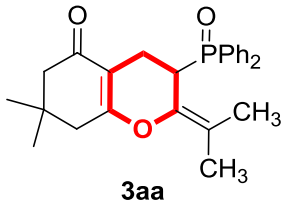
## 5. Characterizations of Substrate, Cyclization Products and Intermediates

*Diethyl (1-(2,6-dimethylphenoxy)-4-ethylhexa-2,3-dien-2-yl)phosphonate(**1o**)*




Yellow liquid, **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.4 Hz, 2H), 6.93 (dd, *J* = 8.0, 6.8 Hz, 1H), 4.36 (d, *J* = 12.6 Hz, 2H), 4.23-4.12 (m, 4H), 2.32 (s, 6H), 2.19-2.09 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H), 1.12 (t, *J* = 7.4 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 208.81 (d, *J* = 5.5 Hz), 155.4, 131.2, 128.8, 124.0, 111.8 (d, *J* = 15.1 Hz), 93.8 (d, *J* = 194.0 Hz), 69.5 (d, *J* = 12.4 Hz), 62.1 (d, *J* = 5.8 Hz), 25.1 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.7 Hz), 16.2, 12.1 (d, *J* = 2.0 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 17.2 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{20}H_{32}O_4P$ : 367.2033, Found : 367.2028.

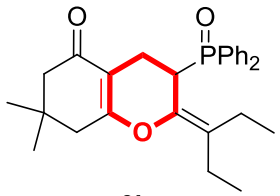
*3-(diphenylphosphoryl)-7,7-dimethyl-2-(propan-2-ylidene)-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3aa**).*




**3aa**

White solid, (122 mg, 97 % yield). *m.p.*: 195.4-196.7 °C. TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.70 (m, 4H), 7.56-7.39 (m, 6H), 3.81 (dd, *J* = 12.0, 7.8 Hz, 1H), 2.99 (dd, *J* = 17.1, 12.1 Hz, 1H), 2.52-2.35 (m, 1H), 2.14-1.98 (m, 4H), 1.71 (d, *J* = 4.8 Hz, 3H), 1.21 (d, *J* = 3.3 Hz, 3H), 1.00 (d, *J* = 7.9 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.0, 167.7, 136.7 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 98.0 Hz), 131.8 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 8.5 Hz), 131.3 (d, *J* = 9.0 Hz), 130.7 (d, *J* = 94.9 Hz), 128.6 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.4 Hz), 116.8 (d, *J* = 9.4 Hz), 107.9, 50.4, 41.5, 33.7 (d, *J* = 67.7 Hz), 31.8, 28.9, 28.1, 18.36 (d, *J* = 2.4 Hz), 18.3, 17.3. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{26}H_{29}NaO_3P$ : 443.1747, Found : 443.1749.

*3-(Diphenylphosphoryl)-7,7-dimethyl-2-(pentan-3-ylidene)-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one(**3ba**).*

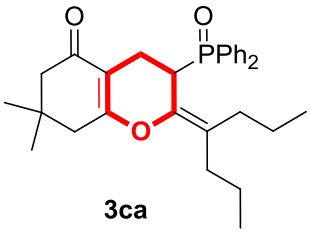



**3ba**

White solid, *m.p.*: 175.3-177.0 °C (109 mg, 81 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.72 (m, 4H), 7.59-7.41 (m, 6H), 3.77 (dd, *J* = 11.4, 8.0 Hz, 1H), 3.03 (dd, *J* = 16.9, 11.9 Hz, 1H), 2.53-2.37 (m, 1H), 2.28 (dd, *J* = 12.7, 5.6 Hz, 1H), 2.18-2.01 (m, 5H), 1.77-1.64 (m, 1H), 1.56-1.47 (m, 1H), 1.03 (d, *J* = 8.9 Hz, 6H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.74 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ

197.1, 168.2, 136.9 (d, *J* = 9.8 Hz), 132.4, 132.0 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 8.5 Hz), 131.4 (d, *J* = 9.0 Hz), 130.7 (d, *J* = 94.9 Hz) ,128.6 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.6 Hz), 127.8 (d, *J* = 9.3 Hz), 108.1, 50.4, 41.5, 33.7 (d, *J* = 67.7 Hz), 31.9, 29.7, 28.5 (d, *J* = 57.6 Hz), 22.8 (d, *J* = 1.9 Hz), 21.6 (d, *J* = 1.6 Hz), 19.0 (d, *J* = 1.3 Hz), 12.6 (d, *J* = 4.3 Hz), 12.4 (d, *J* = 2.6 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.0 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{28}H_{33}NaO_3P$ : 471.2060, Found : 471.2060.

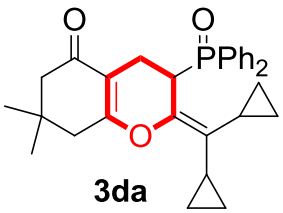
*3-(Diphenylphosphoryl)-2-(heptan-4-ylidene)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one(**3ca**).*




**3ca**

White solid, *m.p.*: 168.7-169.2 ºC (121 mg, 85 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.71 (m, 4H), 7.59-7.39 (m, 6H), 3.80 (dd, *J* = 11.6, 7.9 Hz, 1H), 3.03 (dd, *J* = 17.0, 11.7 Hz, 1H), 2.51-2.35 (m, 1H), 2.26-2.10 (m, 5H), 2.03-1.95 (m, 2H), 1.71-1.62 (m, 1H), 1.55-1.46 (m, 1H), 1.44-1.35 (m, 1H), 1.23-1.15 (m, 1H), 1.14-1.06 (m, 1H), 1.02 (d, *J* = 7.9 Hz, 6H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.1, 168.2, 138.0 (d, *J* = 9.6 Hz), 132.0 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 98.0 Hz), 131.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 8.4 Hz), 131.4 (d, *J* = 9.1 Hz), 130.9 (d, *J* = 99.0 Hz), 128.6 (d, *J* = 11.4 Hz), 128.3 (d, *J* = 11.5 Hz), 125.0 (d, *J* = 9.2 Hz), 108.1, 50.4, 41.5, 33.8 (d, *J* = 67.7 Hz), 32.2 (d, *J* = 1.8 Hz), 31.9, 30.9 (d, *J* = 1.9 Hz), 28.8, 28.1, 21.3 (d, *J* = 3.03 Hz), 20.9 (d, *J* = 2.02 Hz), 19.1, 14.3, 14.1. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.7 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{30}H_{37}NaO_3P$ : 499.2373, Found : 499.2373.

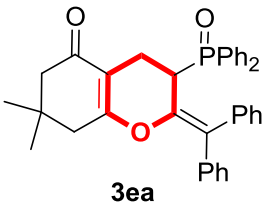
*2-(Dicyclopropylmethylene)-3-(diphenylphosphoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-on e (**3da**).*




**3da**

White solid, *m.p.*: 167.8-168.6 ºC (118 mg, 83 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.69 (m, 4H), 7.58-7.37 (m, 6H), 4.37 (dd, *J* = 11.8, 7.8 Hz, 1H), 2.96 (dd, *J* = 17.0, 11.8 Hz, 1H), 2.45-2.34 (m, 1H), 2.21 (dd, *J* = 26.5, 15.8 Hz, 2H), 2.16 -2.03 (m, 2H), 1.63-1.56 (m, 1H), 1.04 (d, *J* = 16.0 Hz, 6H), 0.70-0.46 (m, 6H), 0.36-0.23 (m, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.3, 168.0, 142.2 (d, *J* = 10.3 Hz), 132.6, 132.1 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 8.4 Hz), 131.4 (d, *J* = 9.1 Hz), 130.4, 128.7 (d, *J* = 11.3 Hz), 128.2 (d, *J* = 11.6 Hz), 124.3 (d, *J* = 9.3 Hz), 108.5, 50.4, 41.5, 34.1 (d, *J* = 68.7 Hz), 31.9, 28.6, 28.3, 18.5, 11.3 (d, *J* = 2.4 Hz), 9.8 (d, *J* = 2.4 Hz), 6.3, 5.4 (d, *J* = 2.2 Hz), 5.2 (d, *J* = 1.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{30}H_{33}NaO_3P$ : 495.2060, Found : 495.2059.

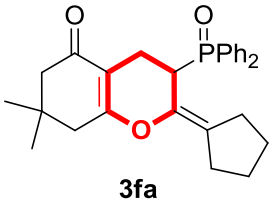
*2-(Diphenylmethylene)-3-(diphenylphosphoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ea**).*




**3ea**

White solid, *m.p.*: 187.9-189.6 ºC (132 mg, 81 % yield). TLC ($R_f$ = 0.50, petroleum ether/ethyl acetate = 1:1). Eluent: 1:2:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.54 (m, 3H), 7.54-7.47 (m, 3H), 7.39 (ddd, *J* = 15.3, 7.7, 2.8 Hz, 4H), 7.31-7.20 (m, 6H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.79 (d, *J* = 6.8 Hz, 2H), 4.02 (dd, *J* = 9.7, 7.6 Hz, 1H), 2.96 (dd, *J* = 16.9, 11.6 Hz, 1H), 2.67-2.49 (m, 1H), 2.34-2.10 (m, 4H), 1.15 (s, 3H), 1.04 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.1, 168.3, 141.5 (d, *J* = 10.1 Hz), 139.1 (d, *J* = 2.2 Hz), 138.2 (d, *J* = 2.5 Hz), 132.3, 132.0 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 4.7 Hz), 131.3 (d, *J* = 5.2 Hz), 130.6 (d, *J* = 96.0 Hz), 130.0, 129.9, 128.7, 128.6, 128.4 (d, *J* = 11.7 Hz), 127.7, 127.5, 127.1, 126.6 (d, *J* = 9.2 Hz), 109.4, 50.5, 41.4, 35.4 (d, *J* = 65.7 Hz), 32.1, 28.6, 28.4, 19.5. **$^{31}$P NMR** (162 MHz, CDCl3) δ 31.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{36}H_{33}NaO_3P$ : 567.2060, Found : 567.2057.

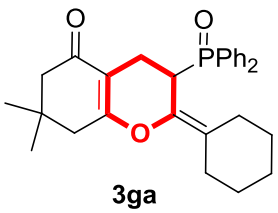
*2-Cyclopentylidene-3-(diphenylphosphoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3fa**).*




**3fa**

White solid, *m.p.*: 219.8-220.6 ºC (112 mg, 84 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.69 (m, 4H), 7.57-7.38 (m, 6H), 3.57 (dd, *J* = 11.7, 8.1 Hz, 1H), 2.97 (dd, *J* = 16.9, 12.4 Hz, 1H), 2.54-2.41 (m, 1H), 2.40-2.43 (m, 2H), 2.15-1.97 (m, 4H), 1.57-1.29 (m, 6H), 1.00 (d, *J* = 7.5 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.1, 167.6, 134.2 (d, *J* = 10.4 Hz), 132.0 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 98.0 Hz), 131.8 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 8.6 Hz), 131.4 (d, *J* = 9.1 Hz), 130.6 (d, *J* = 95.0 Hz), 128.6 (d, *J* = 11.3 Hz), 128.2 (d, *J* = 11.3 Hz), 128.1, 107.9, 50.4, 41.6, 35.7 (d, *J* = 68.7 Hz), 31.8, 28.9 (d, *J* = 3.03 Hz), 28.9, 28.8, 28.0, 26.5, 26.1, 18.0. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{28}H_{31}NaO_3P$ : 469.1903, Found : 469.1907.

*2-Cyclohexylidene-3-(diphenylphosphoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ga**).*

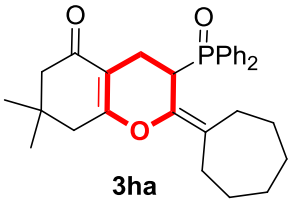



**3ga**

White solid, *m.p.*: 203.5-204.6 ºC (108 mg, 78 % yield). TLC ($R_f$ = 0.10, petroleum ether/ethyl acetate = 1:1).

Eluent: 2:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.68 (m, 4H), 7.56-7.36 (m, 6H), 3.84 (dd, *J* = 11.0, 7.7 Hz, 1H), 3.03-2.91 (m, 1H), 2.50-2.33 (m, 1H), 2.32-2.20 (m, 2H), 2.19-1.99 (m, 4H), 1.86-1.77 (m, 1H), 1.56-1.47 (m, 1H), 1.46-1.30 (m, 4H), 1.29-1.24 (m, 1H), 1.01 (d, *J* = 14.8 Hz, 6H), 0.82-0.79 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.0, 168.1, 134.4 (d, *J* = 9.7 Hz), 132.0 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 98.0 Hz), 131.7 (d, *J* = 2.7 Hz), 131.6 (d, *J* =9.1 Hz), 131.4 (d, *J* = 8.9 Hz), 130.9 (d, *J* = 95.0 Hz), 128.6 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.5 Hz), 124.1 (d, *J* = 9.2 Hz), 107.9, 50.4, 41.5, 33.0 (d, *J* = 68.7 Hz), 31.9, 28.8 (d, *J* = 1.0 Hz), 28.7 (d, *J* = 2.0 Hz), 28.6, 28.4, 26.8 (d, *J* = 1.6 Hz), 26.6 (d, *J* = 2.4 Hz), 26.2, 18.7. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.6 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{29}H_{33}NaO_3P$ : 483.2060, Found : 483.2061.

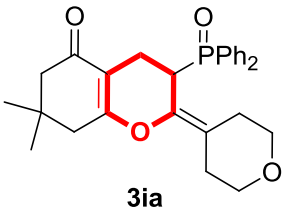
*2-Cycloheptylidene-3-(diphenylphosphoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ha**).*




**3ha**

White solid, *m.p.*: 182.6-183.8 ºC (124 mg, 87 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 2:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.67 (m, 4H), 7.53-7.33 (m, 6H), 3.80 (dd, *J* = 11.7, 7.8 Hz, 1H), 2.95 (dd, *J* = 17.0, 11.9 Hz, 1H), 2.48-2.35 (m, 2H), 2.32-2.22 (m, 1H), 2.10 (s, 2H), 2.06-1.94 (m, 3H), 1.63-1.53 (m, 1H), 1.46-1.41 (m, 2H), 1.40-1.26 (m, 4H), 1.18-1.11 (m, 2H), 0.97 (d, *J* = 10.1 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.0, 168.1, 136.8 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 98.0 Hz), 131.9 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 8.5 Hz), 131.3 (d, *J* = 9.1 Hz), 130.4, 128.5 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.5 Hz), 126.2 (d, *J* = 9.3 Hz), 108.0, 50.4, 41.4, 33.5 (d, *J* =67.7 Hz), 31.8, 29.8, 29.5 (d, *J* = 1.9 Hz), 28.8, 28.7, 28.4(d, *J* = 1.8 Hz), 28.1, 27.2 (d, *J* = 2.0 Hz), 27.1 (d, *J* = 2.0 Hz), 18.8. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.2 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{30}H_{35}NaO_3P$ : 497.2216, Found : 497.2214.

*2-(Dihydro-2H-pyran-4(3H)-ylidene)-3(diphenylphos-phoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ia**).*

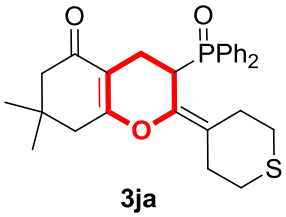



**3ia**

White solid, *m.p.*: 218.4-219.6 ºC (125 mg, 90 % yield). TLC ($R_f$ = 0.10, petroleum ether/ethyl acetate = 1:2). Eluent: 2:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.72 (m, 4H), 7.64-7.41 (m, 6H), 3.81 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.71-3.62 (m, 1H), 3.52-3.43 (m, 2H), 3.00 (dd, *J* = 17.1, 12.1 Hz, 1H), 2.92-2.86 (m, 1H), 2.58-2.32 (m, 3H), 2.23-2.05 (m, 4H), 2.03-1.97 (m, 1H), 1.71-1.62 (m, 1H), 1.06 (d, *J* = 17.1 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.1, 167.7, 135.8 (d, *J* = 9.8 Hz), 132.2 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 98.0 Hz), 131.6 (d, *J* = 8.6 Hz), 131.4 (d, *J* = 9.0 Hz), 130.5 (d, *J* = 94.9 Hz), 128.8 (d, *J* = 11.4 Hz), 128.5 (d, *J* = 11.5 Hz), 118.9 (d, *J* = 9.2 Hz), 108.0, 67.7 (d, *J* = 2.2 Hz), 67.6 (d, *J* = 1.0 Hz), 50.4, 41.4, 33.0 (d, *J* = 67.7 Hz), 31.9, 28.9 (d, *J* = 1.6 Hz),

28.6, 28.3, 27.5 (d, *J* = 1.9 Hz), 18.5. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.7 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{28}H_{31}NaO_4P$ : 485.1852, Found : 485.1853.

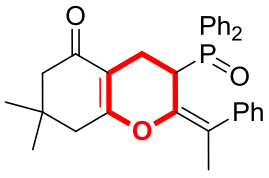
*2-(Dihydro-2H-thiopyran-4(3H)-ylidene)-3(diphenylphos-phoryl)-7,7-dimethyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ja**).*




**3ja**

White solid, *m.p.*: 202.0-203.8 ºC (128 mg, 89 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.71 (m, 4H), 7.57-7.41 (m, 6H), 3.83 (dd, *J* = 10.9, 7.8 Hz, 1H), 2.96 (dd, *J* = 17.0, 12.1 Hz, 1H), 2.86-2.77 (m, 1H), 2.59-2.46 (m, 3H), 2.42-2.28 (m, 2H), 2.19-2.11 (m, 4H), 2.05-1.98 (m, 2H), 1.87-1.78 (m, 1H), 1.02 (d, *J* = 16.6 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.0, 167.7, 136.5 (d, *J* = 9.6 Hz), 132.2 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 90.0 Hz), 131.6 (d, *J* = 8.6 Hz), 131.4 (d, *J* = 9.0 Hz), 130.4 (d, *J* =94.9 Hz), 128.7 (d, *J* = 11.4 Hz), 128.5 (d, *J* = 11.6 Hz), 121.1 (d, *J* = 9.1 Hz), 108.0, 50.4, 41.4, 33.0 (d, *J* = 66.7 Hz), 31.9, 30.4 (d, *J* = 1.6 Hz), 29.1 (d, *J* = 2.9 Hz), 29.0 (d, *J* = 2.0 Hz), 28.7 (d, *J* = 1.6 Hz), 28.6, 28.3, 18.6. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{28}H_{31}NaO_3P$ : 501.1624, Found : 501.1624.

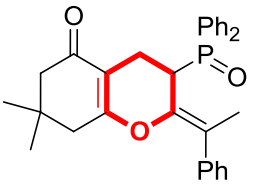
*(E)-3-(diphenylphosphoryl)-7,7-dimethyl-2-(1-phenylethyl-idene)-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ka-E**).*




**3ka-*E***

White solid, *m.p.*: 195.2-196.4 ºC (73 mg, 50 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:2:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.42 (m, 6H), 7.40-7.31 (m, 4H), 7.26-7.20 (m, 3H), 6.83-6.77 (m, 2H), 3.91 (dd, *J* = 10.3, 7.6 Hz, 1H), 2.84 (dd, *J* = 16.9, 11.5 Hz, 1H), 2.53-2.40 (m, 1H), 2.31 (q, *J* = 17.3 Hz, 2H), 2.13 (dd, *J* = 41.8, 16.1 Hz, 2H), 2.00 (d, *J* = 4.5 Hz, 3H), 1.10 (d, *J* = 21.2 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.1, 168.3, 140.1 (d, *J* = 10.2 Hz), 139.9 (d, *J* = 2.3 Hz), 132.3, 131.9 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 8.7 Hz), 131.3 (d, *J* = 8.9 Hz), 130.3, 128.6, 128.5, 128.3 (d, *J* = 11.6 Hz), 128.1 (d, *J* = 1.1 Hz), 127.1, 122.4 (d, *J* = 9.1 Hz), 108.8, 50.5, 41.6, 34.1 (d, *J* = 66.7 Hz), 32.0, 28.7, 28.4, 19.4, 17.9 (d, *J* = 2.1 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.4 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{31}H_{31}NaO_3P$ : 505.1903, Found : 505.1903.

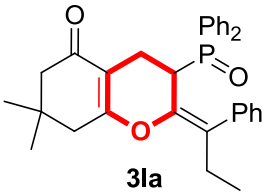
*(Z)-3-(diphenylphosphoryl)-7,7-dimethyl-2-(1-phenylethyl-idene)-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ka-Z**).*



**3ka-*Z***

White solid, *m.p.*: 209.6-211.5 ºC (58 mg, 40 % yield). TLC ($R_f$ = 0.15, petroleum ether/ethyl acetate = 1:1). Eluent: 1:2:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.89 (m, 2H), 7.85-7.77 (m, 2H), 7.64-7.50 (m, 4H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.23 (m, 1H), 7.19-7.10 (m, 2H), 3.92 (dd, *J* = 11.5, 7.7 Hz, 1H), 3.10 (dd, *J* = 17.1, 12.5 Hz, 1H), 2.66-2.53 (m, 1H), 2.18-1.97 (m, 4H), 1.52 (d, *J* = 3.3 Hz, 3H), 1.01 (d, *J* = 7.5 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.1, 167.7, 139.4 (d, *J* = 3.0 Hz), 138.2 (d, *J* = 9.8 Hz), 132.4, 132.2 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 94.9 Hz), 131.4 (d, *J* = 9.2 Hz), 128.8 (d, *J* = 11.1 Hz), 128.4 (d, *J* = 11.6 Hz), 128.3 (d, *J* = 2.5 Hz), 127.9, 126.9, 120.2 (d, *J* = 9.5 Hz), 108.3, 50.4, 41.2, 34.5 (d, *J* = 67.7 Hz), 31.9, 28.6, 28.2, 18.5 (d, *J* = 1.5 Hz), 18.3 (d, *J* = 2.0 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.3 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{31}H_{31}NaO_3P$ : 505.1903, Found : 505.1902.

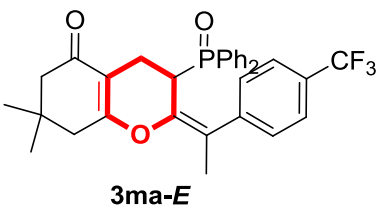
*(E)-3-(diphenylphosphoryl)-7,7-dimethyl-2-(1-phenylpropyl-idene)-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3la**).*



**3la**

White solid, *m.p.*: 170.4-171.8 ºC (97 mg, 65 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.45 (m, 6H), 7.44-7.34 (m, 4H), 7.28-7.18 (m, 3H), 6.68 (d, *J* = 6.6 Hz, 2H), 3.73 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.84 (dd, *J* = 16.9, 11.5 Hz, 1H), 2.67-2.56 (m, 1H), 2.54-2.42 (m, 1H), 2.43-2.27 (m, 3H), 2.17 (q, *J* = 16.1 Hz, 2H), 1.12 (d, *J* = 24.2 Hz, 6H), 0.87 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.2, 168.5, 139.9 (d, *J* = 9.9 Hz), 138.6 (d, *J* = 2.3 Hz), 132.4, 131.9 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.0 Hz), 131.5 (d, *J* = 1.3 Hz), 131.4 (d, *J* = 2.0 Hz), 130.7 (d, *J* = 96.0 Hz), 128.6 (d, *J* = 6.2 Hz), 128.5 (d, *J* = 3.03 Hz), 128.5, 128.3 (d, *J* = 11.7 Hz), 127.1, 109.0, 50.5, 41.6, 34.33 (d, *J* = 66.7 Hz), 32.1, 28.52, 28.50, 24.7 (d, *J* = 1.6 Hz), 19.6 (d, *J* = 1.0 Hz), 12.5 (d, *J* = 3.6 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.4 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{32}H_{33}NaO_3P$ : 519.2060, Found : 519.2061.

*(E)-3-(diphenylphosphoryl)-7,7-dimethyl-2-(1-(4-(trifluoro-methyl)phenyl)ethylidene)-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one (**3ma-E**).*

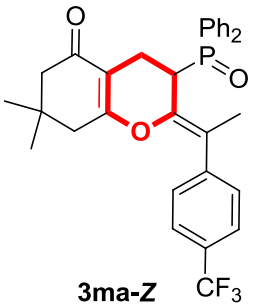


**3ma-*E***

White solid, *m.p.*: 214.8-215.9 ºC (89 mg, 54 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2).

Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.43 (m, 8H), 7.43-7.31 (m, 4H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.82 (dd, *J* = 10.9, 7.1 Hz, 1H), 2.83 (dd, *J* = 17.0, 11.4 Hz, 1H), 2.52-2.36 (m, 1H), 2.34-2.21 (m, 2H), 2.19-2.00 (m, 5H), 1.08 (d, *J* = 15.8 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 196.8, 168.0, 143.8, 140.8 (d, *J* = 10.2 Hz), 132.0 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 98.0 Hz), 131.4 (d, *J* = 8.8 Hz), 131.1 (d, *J* = 9.0 Hz), 130.4 (d, *J* = 96.0 Hz), 128.6 (d, *J* = 8.1 Hz), 128.5, 128.5 (d, *J* = 13.1 Hz), 125.8 (d, *J* = 3.7 Hz), 125.5, 124.1 (q, *J* = 273.7 Hz), 121.2 (d, *J* = 9.0 Hz), 108.6, 50.4, 41.5, 34.3 (d, *J* = 65.7 Hz), 31.9, 28.8, 28.2, 19.2, 17.9 (d, *J* = 1.8 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.7 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{32}H_{30}NaO_3F_3P$ : 573.1777, Found : 573.1773.

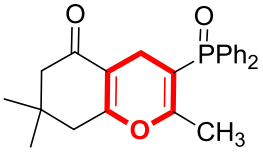
*(Z)-3-(diphenylphosphoryl)-7,7-dimethyl-2-(1-(4-(trifluoro-methyl)phenyl)ethylidene)-3,4,7,8-tetrahydro-2H -chromen-5(6H)-one (**3ma-Z**).*




**3ma-*Z***

White solid, *m.p.*: 228.6-229.9 ºC (63 mg, 38 % yield). TLC ($R_f$ = 0.15, petroleum ether/ethyl acetate = 1:2). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.76 (m, 4H), 7.62-7.52 (m, 6H), 7.48-7.44 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.94 (dd, *J* = 11.1, 7.8 Hz, 1H), 3.08 (dd, *J* = 17.1, 12.7 Hz, 1H), 2.66-2.50 (m, 1H), 2.18-2.07 (m, 3H), 2.03-1.95 (m, 1H), 1.54 (d, *J* = 3.3 Hz, 3H), 1.02 (d, *J* = 14.3 Hz, 6H).**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.0, 167.3, 143.2, 139.4 (d, *J* = 9.8 Hz), 132.3 (d, *J* = 1.4 Hz), 132.1 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 8.5 Hz), 131.3 (d, *J* = 9.1 Hz), 130.2 (d, *J* = 96.0 Hz), 129.0, 128.8 (d, *J* = 11.5 Hz), 128.6 (d, *J* = 2.4 Hz), 128.5 (d, *J* = 11.6 Hz), 124.9 (d, *J* = 3.8 Hz), 124.8 (d, *J* = 11.1 Hz), 124.2 (q, *J* = 273.7 Hz), 118.8 (d, *J* = 9.4 Hz), 108.4, 50.4, 41.2, 34.4 (d, *J* = 66.7 Hz), 32.0, 28.5, 28.2, 18.4 (d, *J* = 1.5 Hz), 18.1 (d, *J* = 2.0 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.6 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{32}H_{30}NaO_3F_3P$ : 573.1777, Found : 573.1777.

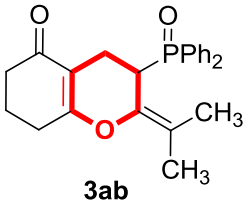
*3-(Diphenylphosphoryl)-2,7,7-trimethyl-7,8-dihydro-4H-chromen-5(6H)-one (**3na**).*




**3na**

White solid, *m.p.*: 148.6-149.9 ºC (100 mg, 85 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 2:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.67 (m, 4H), 7.57-7.45 (m, 6H), 2.51 (d, *J* = 1.5 Hz, 2H), 2.31 (s, 2H), 2.27 (s, 3H), 2.23 (s, 2H), 1.07 (s, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.5, 164.0, 158.6 (d, *J* = 17.6 Hz), 132.1, 132.1 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 9.9 Hz), 131.1, 128.8 (d, *J* = 12.2 Hz), 108.3 (d, *J* = 9.0 Hz), 101.7 (d, *J* = 30.3 Hz), 50.6, 40.8, 32.0, 29.7, 28.4, 21.2 (d, *J* = 10.6 Hz), 18.7 (d, *J* = 3.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.7 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{24}H_{25}NaO_3P$ : 415.1434, Found : 415.1433.

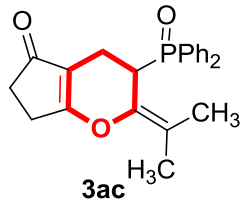
*3-(Diphenylphosphoryl)-2-(propan-2-ylidene)-3,4,7,8-tetra-hydro-2H-chromen-5(6H)-one (**3ab**).*




**3ab**

White solid, *m.p.*: 205.2-206.8 ºC (105 mg, 89 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:5). Eluent: 4:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.69 (m, 4H), 7.52-7.36 (m, 6H), 3.81 (dd, *J* = 13.8, 7.9 Hz, 1H), 3.00 (dd, *J* = 17.1, 12.2 Hz, 1H), 2.46-2.29 (m, 1H), 2.24-2.13 (m, 2H), 2.11-2.00 (m, 2H), 1.79-1.72 (m, 1H), 1.69 (d, *J* = 4.7 Hz, 3H), 1.66-1.55 (m, 1H), 1.24 (d, *J* = 2.9 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.0, 169.0, 136.5 (d, *J* = 9.7 Hz), 132.0 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 97.0 Hz), 131.7 (d, *J* = 9.1 Hz), 131.3 (d, *J* = 9.0 Hz), 130.5 (d, *J* = 96.0 Hz), 128.3 (d, *J* = 24.2 Hz), 128.3, 117.0 (d, *J* = 9.5 Hz), 109.1, 36.3, 33.8 (d, *J* = 68.7 Hz), 27.6, 20.3, 18.4, 18.3, 17.3 (d, *J* = 2.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.0 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{24}H_{25}NaO_3P$ : 415.1439, Found : 415.1437.

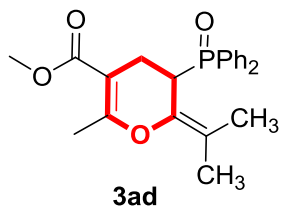
*3-(Diphenylphosphoryl)-2-(propan-2-ylidene)-3,4,6,7-tetra-hydrocyclopenta[b]pyran-5(2H)-one (**3ac**).*




**3ac**

White solid, *m.p.*: 210.4-211.8 ºC (97 mg, 85 % yield). TLC ($R_f$ = 0.10, petroleum ether/ethyl acetate = 1:5). Eluent: 5:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.68 (m, 4H), 7.57-7.38 (m, 6H), 3.82 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.82 (dd, *J* = 16.8, 11.9 Hz, 1H), 2.51-2.37 (m, 2H), 2.31-2.16 (m, 2H), 2.15-2.03 (m, 1H), 1.75 (d, *J* = 4.7 Hz, 3H), 1.29 (d, *J* = 3.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 202.4, 181.9, 137.9 (d, *J* = 10.0 Hz), 132.2 (d, *J* = 2.7 Hz), 132.0 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 8.5 Hz), 131.3 (d, *J* = 9.1 Hz), 131.0, 130.0 (d, *J* = 94.9 Hz), 128.5 (d, *J* = 11.4 Hz), 128.3 (d, *J* = 11.5 Hz), 119.3 (d, *J* = 9.4 Hz), 112.8, 33.3, 32.8 (d, *J* = 66.7 Hz), 25.7, 18.8 (d, *J* = 2.2 Hz), 17.5 (d, *J* = 21.2 Hz), 17.4. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.5 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{23}H_{23}NaO_3P$ : 401.1277, Found : 401.1277.

*Methyl 3-(diphenylphosphoryl)-6-methyl-2-(propan-2-ylidene) -3,4-dihydro-2H-pyran-5-carboxylate(**3ad**).*

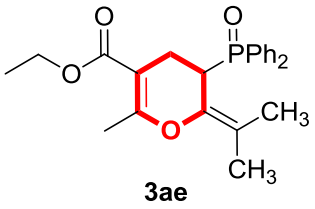



**3ad**

White solid, *m.p.*: 159.5-160.8 ºC (100 mg, 84 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:3). Eluent: 3:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.75 (m, 4H), 7.60-7.39 (m, 6H), 3.76 (dd, *J* = 14.1, 7.5 Hz, 1H), 3.63 (s, 3H), 3.14 (dd, *J* = 17.3, 11.8

Hz, 1H), 2.63-2.49 (m, 1H), 2.00 (s, 3H), 1.72 (d, *J* = 5.0 Hz, 3H), 1.23 (d, *J* = 3.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.6, 163.2, 136.9 (d, *J* = 9.1 Hz), 132.0 (d, *J* = 2.8 Hz), 131.8, 131.7 (d, *J* = 8.6 Hz), 131.5 (d, *J* = 9.1 Hz), 131.4, 130.8 (d, *J* = 59.6 Hz), 128.4 (d, *J* = 11.3 Hz), 128.1 (d, *J* = 11.5 Hz), 115.2 (d, *J* = 9.8 Hz), 99.4, 51.1, 34.6 (d, *J* = 58.6 Hz), 21.8 (d, *J* = 1.4 Hz), 19.4, 18.2 (d, *J* = 2.4 Hz), 17.2 (d, *J* = 2.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.1 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{23}H_{25}NaO_4P$ : 419.1383, Found : 419.1384.

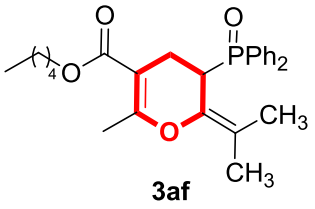
*Ethyl 3-(diphenylphosphoryl)-6-methyl-2-(propan-2-ylidene) -3,4-dihydro-2H-pyran-5-carboxylate (**3ae**).*




**3ae**

White solid, *m.p.*: 178.5-160.8 ºC (109 mg, 89 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.74 (m, 4H), 7.57-7.38 (m, 6H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.74 (dd, *J* = 14.3, 7.5 Hz, 1H), 3.13 (dd, *J* = 17.3, 11.8 Hz, 1H), 2.61-2.47 (m, 1H), 1.97 (s, 3H), 1.70 (d, *J* = 5.0 Hz, 3H), 1.22-1.19 (m, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 162.9, 137.0 (d, *J* = 9.0 Hz), 131.9 (d, *J* = 2.7 Hz), 131.7, 131.7 (d, *J* = 8.5 Hz), 131.7 (d, *J* = 65.7 Hz), 131.5 (d, *J* = 9.0 Hz), 130.8 (d, *J* = 65.7 Hz), 128.3 (d, *J* = 11.3 Hz), 128.1 (d, *J* = 11.6 Hz), 115.1 (d, *J* = 9.8 Hz), 99.7, 59.7, 34.7 (d, *J* = 68.7 Hz), 21.8, 19.4, 18.21 (d, *J* = 2.4 Hz), 17.18 (d, *J* = 2.2 Hz), 14.4. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.0 (s). **HRMS (ESI):** ($[M+H]^+$) Calcd for $C_{24}H_{28}O_4P$: 411.1720, Found: 411.1739.

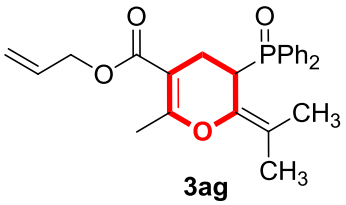
*Pentyl 3-(diphenylphosphoryl)-6-methyl-2-(propan-2-ylide-ne)-3,4-dihydro-2H-pyran-5-carboxylate (**3af**).*




**3af**

White solid, *m.p.*: 166.3-168.1 ºC (113 mg, 92 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.75 (m, 4H), 7.58-7.39 (m, 6H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.75 (dd, *J* = 14.5, 7.6 Hz, 1H), 3.14 (dd, *J* = 17.3, 11.9 Hz, 1H), 2.63-2.49 (m, 1H), 1.98 (s, 3H), 1.72 (d, *J* = 5.0 Hz, 3H), 1.65-1.54 (m, 2H), 1.34-1.29 (m, 4H), 1.23 (d, *J* = 3.4 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 162.8, 136.9 (d, *J* = 9.0 Hz), 131.9 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 8.3 Hz), 131.8, 131.7 (d, *J* = 69.7 Hz), 131.5 (d, *J* = 9.0 Hz), 130.8 (d, *J* = 69.7 Hz), 128.3 (d, *J* = 11.3 Hz), 128.2 (d, *J* = 11.5 Hz), 115.2 (d, *J* = 9.7 Hz), 99.7, 64.0, 34.7 (d, *J* = 68.7 Hz), 28.4, 28.2, 22.3, 21.8 (d, *J* = 1.3 Hz), 19.4, 18.2 (d, *J* = 2.3 Hz), 17.2 (d, *J* = 2.3 Hz), 14.0. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.0 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{27}H_{33}NaO_4P$ : 475.2009, Found : 475.2012.

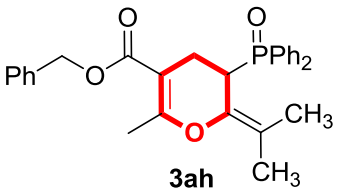
*Allyl 3-(diphenylphosphoryl)-6-methyl-2-(propan-2-ylidene) -3,4-dihydro-2H-pyran-5 carboxylate (**3ag**).*



**3ag**

White solid, *m.p.*: 169.2-170.4 ºC (118 mg, 93 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.76 (m, 4H), 7.59-7.54 (m, 1H), 7.52-7.48 (m, 3H), 7.45-7.40 (m, 2H), 5.97-5.83 (m, 1H), 5.28-5.17 (m, 2H), 4.56-4.53 (m, 2H), 3.76 (dd, *J* = 14.2, 7.5 Hz, 1H), 3.17 (dd, *J* = 17.3, 11.7 Hz, 1H), 2.65-2.51 (m, 1H), 2.00 (s, 3H), 1.72 (d, *J* = 5.0 Hz, 3H), 1.24 (d, *J* = 3.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.7, 163.4, 137.0 (d, *J* = 8.9 Hz), 132.8, 132.0 (d, *J* = 2.9 Hz), 131.8, 131.7 (d, *J* = 8.6 Hz), 131.7 (d, *J* = 62.6 Hz), 131.5 (d, *J* = 9.1 Hz), 130.7 (d, *J* = 61.6 Hz), 128.4 (d, *J* = 11.3 Hz), 128.2 (d, *J* = 11.6 Hz), 117.3, 115.3 (d, *J* = 9.5 Hz), 99.4, 64.4, 34.67 (d, *J* = 68.7 Hz), 21.8 (d, *J* = 1.4 Hz), 19.4, 18.2 (d, *J* = 2.3 Hz), 17.2 (d, *J* = 2.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.0 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{25}H_{27}NaO_4P$ : 445.1539, Found : 445.1541.

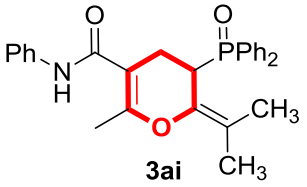
*Benzyl 3-(diphenylphosphoryl)-6-methyl-2-(propan-2-ylide-ne)-3,4-dihydro-2H-pyran-5-carboxylate (**3ah**).*



**3ah**

White solid, *m.p.*: 182.1-183.6 ºC (127 mg, 90 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 2:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.91-7.83 (m, 2H), 7.82-7.74 (m, 2H), 7.55- 7.42 (m, 4H), 7.39-7.27 (m, 7H), 5.08 (s, 2H), 3.75 (dd, *J* = 14.2, 7.5 Hz, 1H), 3.20 (dd, *J* = 17.3, 11.7 Hz, 1H), 2.68-2.49 (m, 1H), 1.99 (s, 3H), 1.71 (d, *J* = 4.9 Hz, 3H), 1.23 (d, *J* = 3.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.8, 163.58, 137.0 (d, *J* = 9.0 Hz), 136.7, 132.0 (d, *J* = 2.7 Hz), 131.8, 131.7 (d, *J* = 68.7 Hz), 131.6 (d, *J* = 20.2 Hz), 131.4, 130.7 (d, *J* = 67.7 Hz), 128.4, 128.4 (d, *J* = 11.5 Hz), 128.2 (d, *J* = 11.5 Hz), 127.8, 115.3 (d, *J* = 9.7 Hz), 99.3, 65.5, 34.7 (d, *J* = 67.7 Hz), 21.8 (d, *J* = 1.1 Hz), 19.5, 18.2 (d, *J* = 2.3 Hz), 17.2 (d, *J* = 2.2 Hz). **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 28.9 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{29}H_{29}NaO_4P$ : 495.1696, Found : 495.1700.

*3-(Diphenylphosphoryl)-6-methyl-N-phenyl-2-(propan-2-ylidene)-3,4-dihydro-2H-pyran-5-carboxamide (**3ai**).*

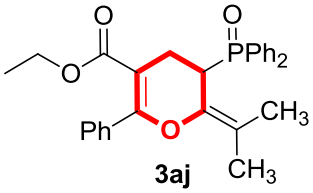


**3ai**

White solid, *m.p.*: 190.2-191.8 ºC (121 mg, 88 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:2). Eluent: 2:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.90-7.82 (m, 2H), 7.75-7.71 (m, 4H), 7.60-7.43 (m, 6H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.08-4.00 (m, 1H), 3.18 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.80-2.69 (m, 1H), 1.69 (d, *J* = 5.4 Hz, 3H), 1.48 (d,

*J* = 1.7 Hz, 3H), 1.34 (d, *J* = 3.8 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 168.0, 154.3, 139.5, 138.1 (d, *J* = 8.5 Hz), 132.7 (d, *J* =97.0 Hz), 132.4 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 8.5 Hz), 131.1 (d, *J* = 9.4 Hz), 129.3 (d, *J* = 96.0 Hz), 129.0 (d, *J* = 11.6 Hz), 128.9, 128.2 (d, *J* = 11.5 Hz), 123.4, 119.4, 111.8 (d, *J* = 10.6 Hz), 105.2 (d, *J* = 2.5 Hz), 35.3 (d, *J* = 70.7 Hz), 24.4 (d, *J* = 2.9 Hz), 18.4 (d, *J* = 2.4 Hz), 16.9 (d, *J* = 2.5 Hz), 16.5. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.4 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{28}H_{28}NNaO_3P$ : 480.1704, Found : 480.1701.

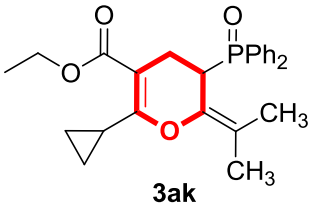
*Ethyl 3-(diphenylphosphoryl)-6-phenyl-2-(propan-2-ylidene) -3,4-dihydro-2H-pyran-5-carboxylate (**3aj**).*



**3aj**

White solid, *m.p.*: 158.6-159.9 ºC (132 mg, 93 % yield). TLC ($R_f$ = 0.10, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 7.83-7.76 (m, 2H), 7.59-7.55 (m, 1H), 7.53-7.45 (m, 3H), 7.40-7.27 (m, 5H), 7.18-7.12 (m, 2H), 3.92-3.79 (m, 3H), 3.33 (dd, *J* = 17.9, 12.3 Hz, 1H), 2.81-2.68 (m, 1H), 1.74 (d, *J* = 4.9 Hz, 3H), 1.23 (d, *J* = 3.4 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 161.3, 137.25 (d, *J* = 9.2 Hz), 135.8, 132.0 (d, *J* = 2.7 Hz), 131.82, 131.76, 131.7 (d, *J* = 96.0 Hz), 131.5 (d, *J* = 9.1 Hz), 130.7 (d, *J* = 95.0 Hz), 129.0, 128.8, 128.5 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.6 Hz), 127.3, 116.0 (d, *J* = 9.7 Hz), 101.9, 59.8, 34.7 (d, *J* = 68.7 Hz), 22.8, 18.3 (d, *J* = 2.3 Hz), 17.4 (d, *J* = 2.1 Hz), 13.7. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 30.0 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{29}H_{29}NaO_4P$ : 495.1696, Found : 495.1696.

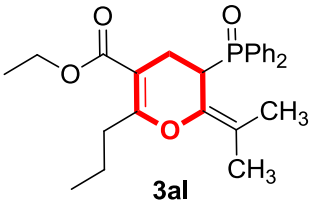
*Ethyl 6-cyclopropyl-3-(diphenylphosphoryl)-2-(propan-2-ylidene)-3,4-dihydro-2H-pyran-5-carboxylate (**3ak**).*



**3ak**

White solid, *m.p.*: 165.4-166.9 ºC (106 mg, 81 % yield). TLC ($R_f$ = 0.10, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.69 (m, 4H), 7.58-7.36 (m, 6H), 4.07 (q, *J* = 6.9 Hz, 2H), 3.75 (dd, *J* = 14.5, 7.7 Hz, 1H), 3.12 (dd, *J* = 17.3, 12.2 Hz, 1H), 2.90-2.75 (m, 1H), 2.63-2.49 (m, 1H), 1.59 (d, *J* = 4.9 Hz, 3H), 1.23 (d, *J* = 3.4 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.90-0.80 (m, 2H), 0.75-0.70 (m, 1H), 0.58-0.53 (m, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.8, 136.3 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 8.4 Hz), 131.8, 131.6 (d, *J* = 81.8 Hz), 131.4 (d, *J* = 9.1 Hz), 130.7 (d, *J* = 81.8 Hz), 128.3 (d, *J* = 21.2 Hz), 128.2 (d, *J* = 1.7 Hz), 114.9 (d, *J* = 9.7 Hz), 99.1, 59.7, 34.8 (d, *J* = 68.7 Hz), 22.4, 18.3 (d, *J* = 2.3 Hz), 16.8 (d, *J* = 2.3 Hz), 14.4, 11.9, 7.3, 6.2. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.7 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{26}H_{29}NaO_4P$ : 459.1696, Found : 459.1699.

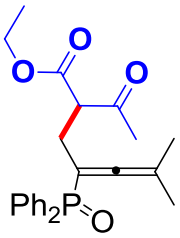
*Ethyl 3-(diphenylphosphoryl)-2-(propan-2-ylidene)-6-propyl-3,4-dihydro-2H-pyran-5-carboxylate (**3al**).*



**3al**

White solid, *m.p.*: 159.7-160.7 $^{o}$C (125 mg, 95 % yield). TLC ($R_f$ = 0.20, petroleum ether/ethyl acetate = 1:1). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.84 (m, 2H), 7.80-7.73 (m, 2H), 7.60-7.53 (m, 1H), 7.53-7.45 (m, 3H), 7.43-7.38 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.74 (dd, *J* = 13.6, 7.7 Hz, 1H), 3.11 (dd, *J* = 17.4, 12.2 Hz, 1H), 2.77-2.70 (m, 1H), 2.64-2.50 (m, 1H), 2.13-2.00 (m, 1H), 1.70 (d, *J* = 5.0 Hz, 3H), 1.58-1.47 (m, 2H), 1.23-1.20 (m, 6H), 0.92 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 166.4, 136.9 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 8.3 Hz), 131.8, 131.7 (d, *J* = 90.9 Hz), 131.5 (d, *J* = 9.1 Hz), 130.8 (d, *J* = 89.9Hz), 128.4 (d, *J* = 11.3 Hz), 128.1 (d, *J* = 11.5 Hz), 115.0 (d, *J* = 9.6 Hz), 99.4, 59.7, 34.5 (d, *J* = 68.7 Hz), 34.4, 22.0, 20.7, 18.2 (d, *J* = 2.4 Hz), 17.1 (d, *J* = 2.3 Hz), 14.3, 14.1. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 29.7 (s). **HRMS (ESI):** ($[M+Na]^+$) Calcd for $C_{26}H_{31}NaO_4P$ : 461.1852, Found : 461.1854.

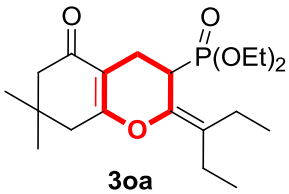
*Ethyl 2-acetyl-4-(diphenylphosphoryl)-6-methyl-hepta-4,5-dienoate (**3ae'**).*



**3ae'**

Yellow liquid, (112 mg, 91 % yield). TLC ($R_f$ = 0.15, petroleum ether/ethyl acetate = 1:2). Eluent: 1:1:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.60 (m, 4H), 7.47-7.35 (m, 6H), 4.14-4.01 (m, 2H), 3.74 (t, *J* = 7.3 Hz, 1H), 2.79-2.69 (m, 2H), 2.16 (s, 3H), 1.32 (dd, *J* = 5.9, 4.6 Hz, 6H), 1.17 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 207.0 (d, *J* = 6.3 Hz), 202.1, 168.7, 132.3 (d, *J* = 5.4 Hz), 131.8 (d, *J* = 2.3 Hz), 131.5 (d, *J* = 3.7 Hz), 131.4 (d, *J* = 3.6 Hz), 131.2 (d, *J* = 5.4 Hz), 128.3 (d, *J* = 2.2 Hz), 128.2 (d, *J* = 2.2 Hz), 100.5 (d, *J* = 13.8 Hz), 94.7, 93.6, 61.5, 58.1 (d, *J* = 6.8 Hz), 29.3, 26.4 (d, *J* = 10.4 Hz), 19.0, 19.0 (d, *J* = 11.3 Hz), 14.0. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 31.6 (s). **HRMS** (ESI): ($[M+Na]^+$) Calcd for $C_{24}H_{27}NaO_4P$: 433.1539, Found: 433.1533.

*Diethyl(7,7-dimethyl-5-oxo-2-(pentan-3-ylidene)-3,4,5,6,7,8-hexahydro-2H-chromen-3-yl)phosphonate(**3oa**)*

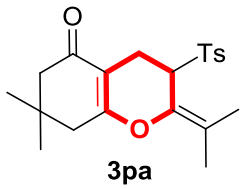


**3oa**

Yellow liquid, (95 mg, 82 % yield). TLC ($R_f$ = 0.3, petroleum ether/ethyl acetate = 1:1). Eluent: 1:2:1 (v/v/v) of ethyl acetate/petroleum ether/dichloromethane. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 4.11-3.97 (m, 4H), 3.37 (dd, *J* = 22.7, 7.1 Hz, 1H), 3.01 (dd, *J* = 16.4, 12.9 Hz, 1H), 2.42-2.25 (m, 4H), 2.23-2.10 (m, 4H), 2.04-1.94 (m, 1H), 1.26 (td, *J* = 7.0, 4.7 Hz, 6H), 1.09 (d, *J* = 14.8 Hz, 6H), 1.00 (td, *J* = 7.5, 3.6 Hz, 6H). **$^{13}$C NMR**

(100 MHz, $CDCl_3$) δ 197.1, 167.7, 136.8 (d, *J* = 12.3 Hz), 127.2 (d, *J* = 11.8 Hz), 108.0, 62.4 (d, *J* = 7.1 Hz), 62.2 (d, *J* = 7.1 Hz), 50.5, 41.7, 32.2, 30.6 (d, *J* = 143.42 Hz), 29.0, 27.8, 23.0 (d, *J* = 2.4 Hz), 21.7 (d, *J* = 2.3 Hz), 18.6 (d, *J* = 3.9 Hz), 16.45 (d, *J* = 10.4 Hz), 16.45, 12.71 (d, *J* = 9.2 Hz), 12.70. **$^{31}$P NMR** (162 MHz, $CDCl_3$) δ 23.4 (s). **HRMS** (ESI): ($[M+H]^+$) Calcd for $C_{20}H_{34}O_5P$: 385.2138, Found: 385.2130.

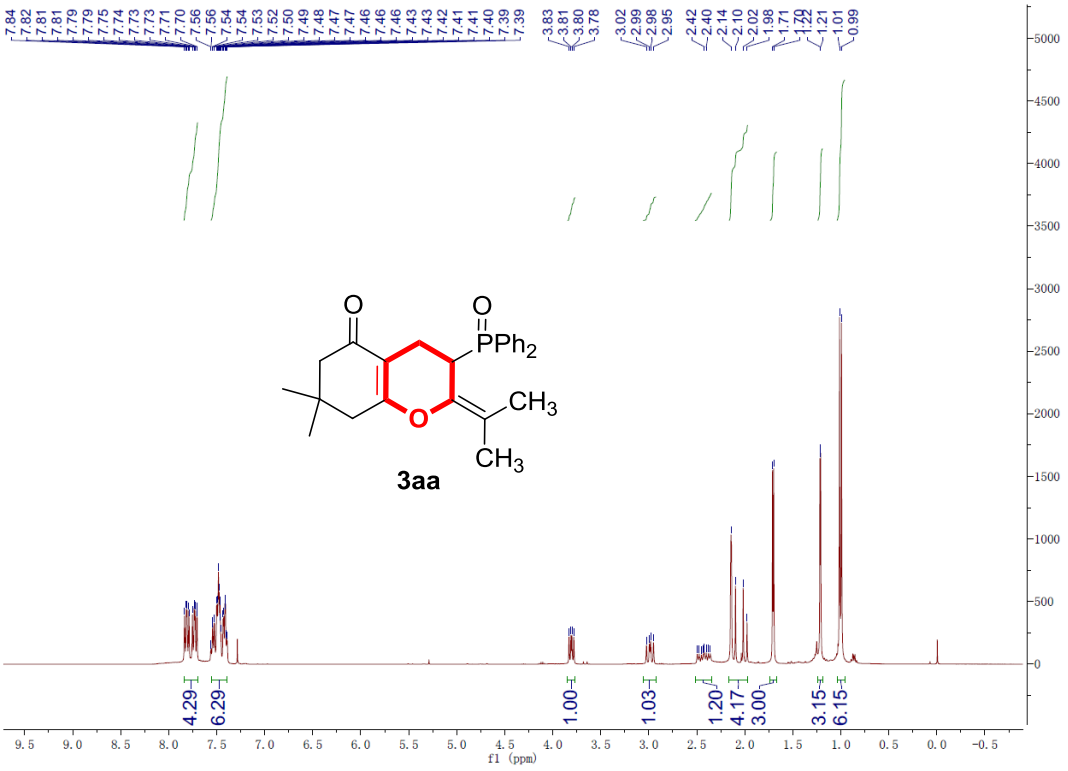
*7,7-dimethyl-2-(propan-2-ylidene)-3-tosyl-3,4,7,8-tetrahydro-2H-chromen-5(6H)-one(**3pa**)*

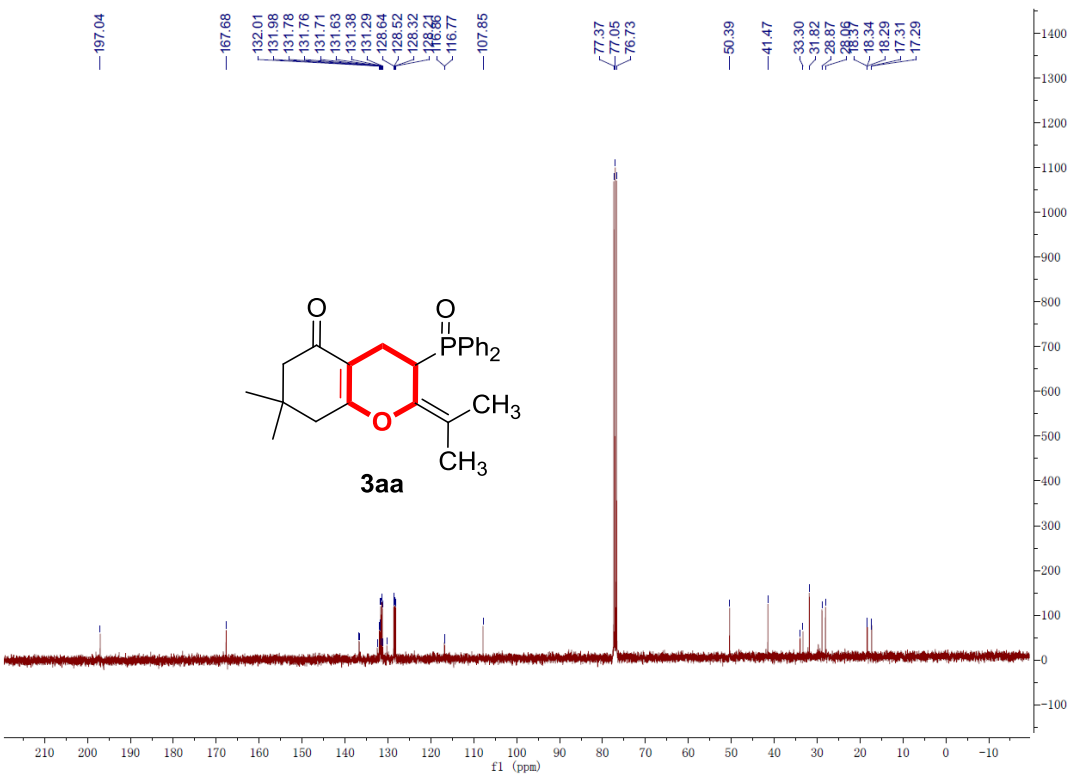



**3pa**

White liquid, (90 mg, 80 % yield). TLC ($R_f$ = 0.1, petroleum ether/ethyl acetate = 4:1). Eluent: 1:3 (v/v) of ethyl acetate/petroleum ether. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.36 (d, *J* = 7.4 Hz, 1H), 3.24 (d, *J* = 18.2 Hz, 1H), 2.42 (s, 3H), 2.41-2.32 (m, 1H), 2.22-2.04 (m, 4H), 1.77 (s, 3H), 1.49 (s, 3H), 1.02 (d, *J* = 6.8 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 196.6, 166.5), 144.8, 134.9, 134.0, 129.6, 129.1, 121.8, 106.5, 57.7, 50.4, 41.4, 31.8, 28.35, 28.34, 21.6, 18.5, 17.8, 17.6. **HRMS** (ESI): ($[M+H]^+$) Calcd for $C_{21}H_{27}O_4S$: 375.1625, Found: 375.1619.

## 6. $^1$H-NMR, $^{13}$C-NMR, $^{31}$P-NMR, HRMS Spectra for All Products and NOESY for Compound 3ma-*E*




197.04
167.68
132.01
131.98
131.78
131.76
131.71
131.63
131.38
131.29
128.64
128.52
128.32
116.77
107.85
77.37
77.05
76.73
50.39
41.47
33.30
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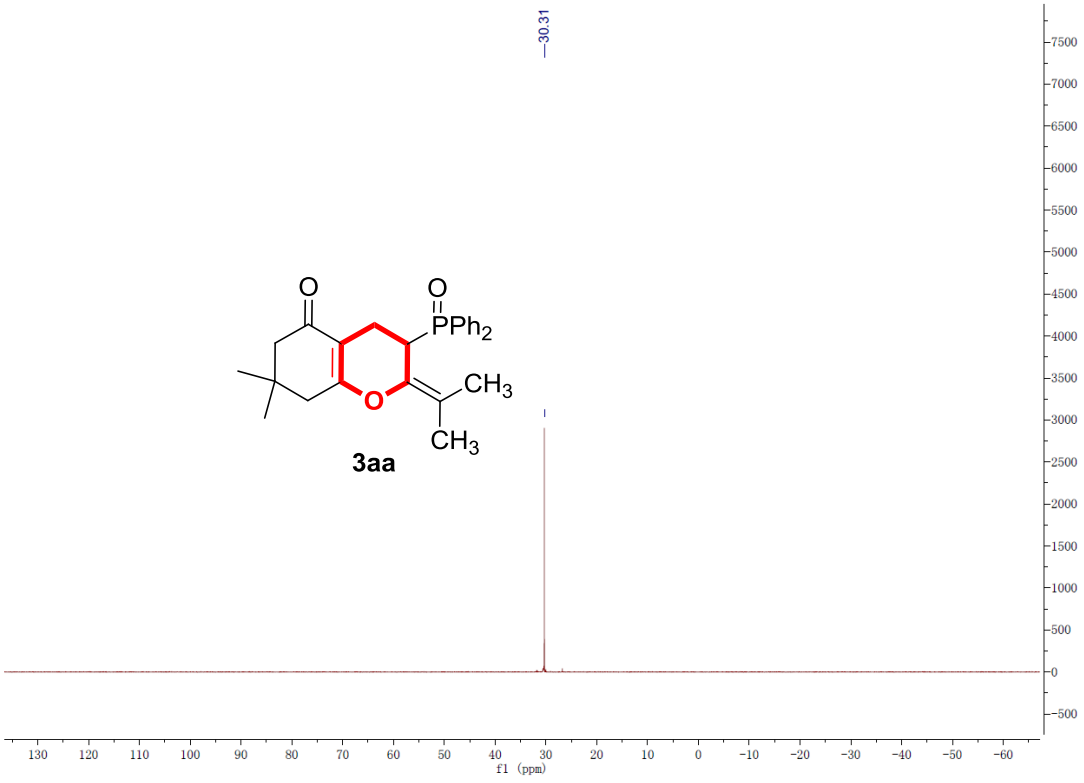
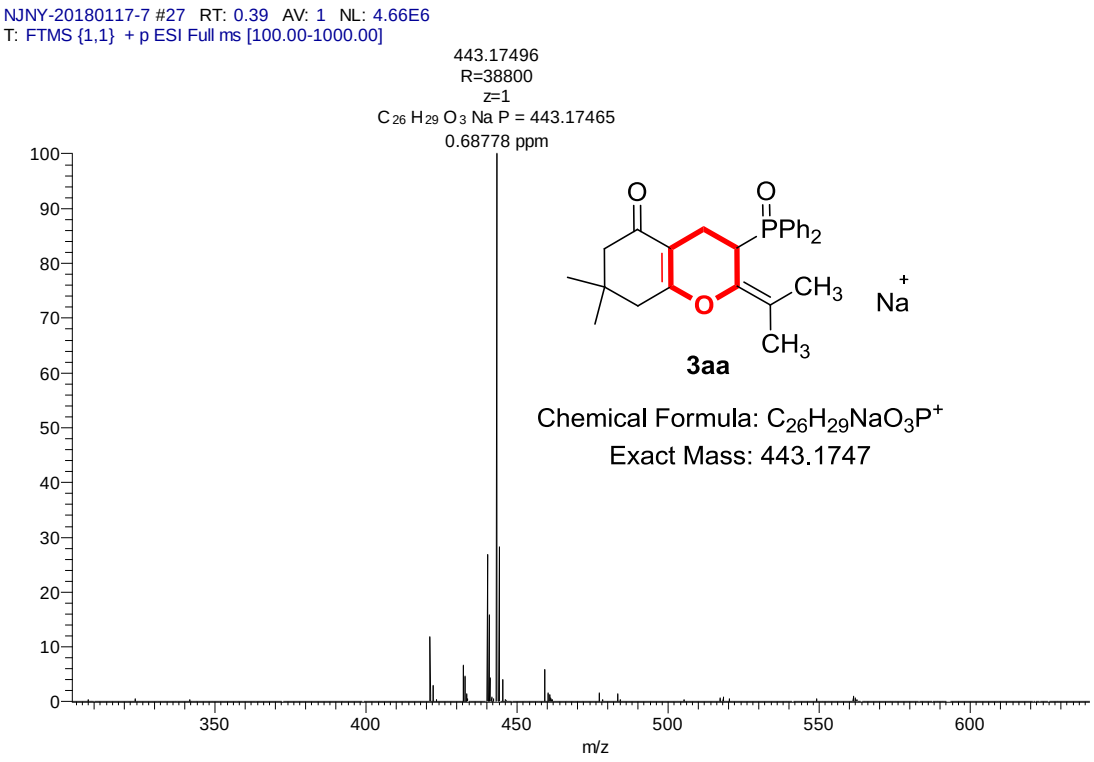
O
PPh2
CH3
CH3
O
3aa
f1 (ppm)


30.31
O
O
PPh2
CH3
CH3
O
3aa
f1 (ppm)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T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
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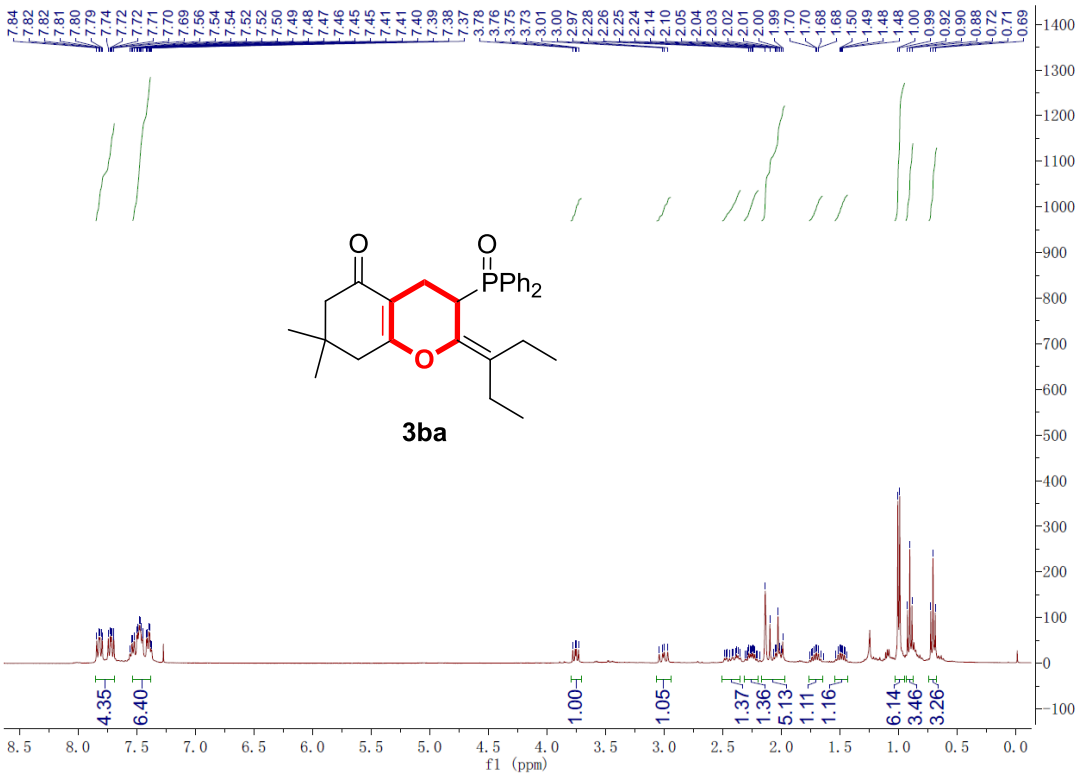
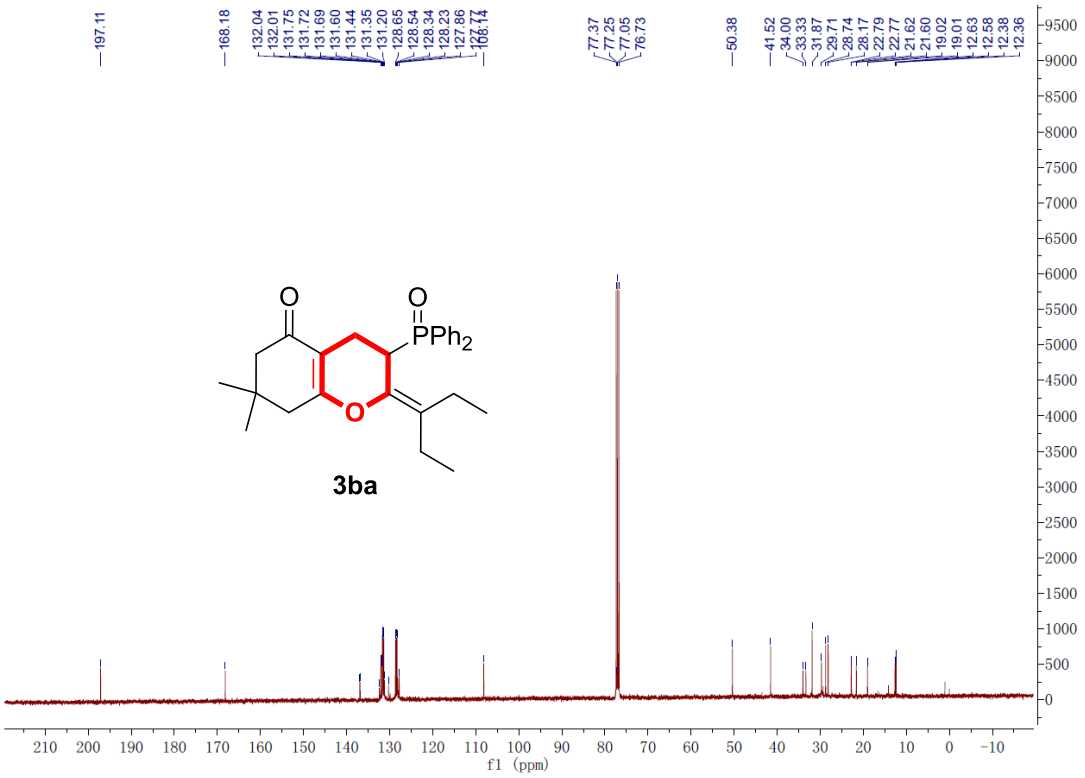
R=38800
z=1
C26 H29 O3 Na P = 443.17465
0.68778 ppm
m/z
3aa
Chemical Formula: C26H29NaO3P+
Exact Mass: 443.1747


3ba
f1 (ppm)


197.11
168.18
132.04
132.01
131.75
131.72
131.69
131.60
131.44
131.35
131.20
128.65
128.54
128.34
128.23
127.86
77.37
77.25
77.05
76.73
50.38
41.52
34.00
33.33
31.87
29.71
28.74
28.17
22.79
22.77
21.62
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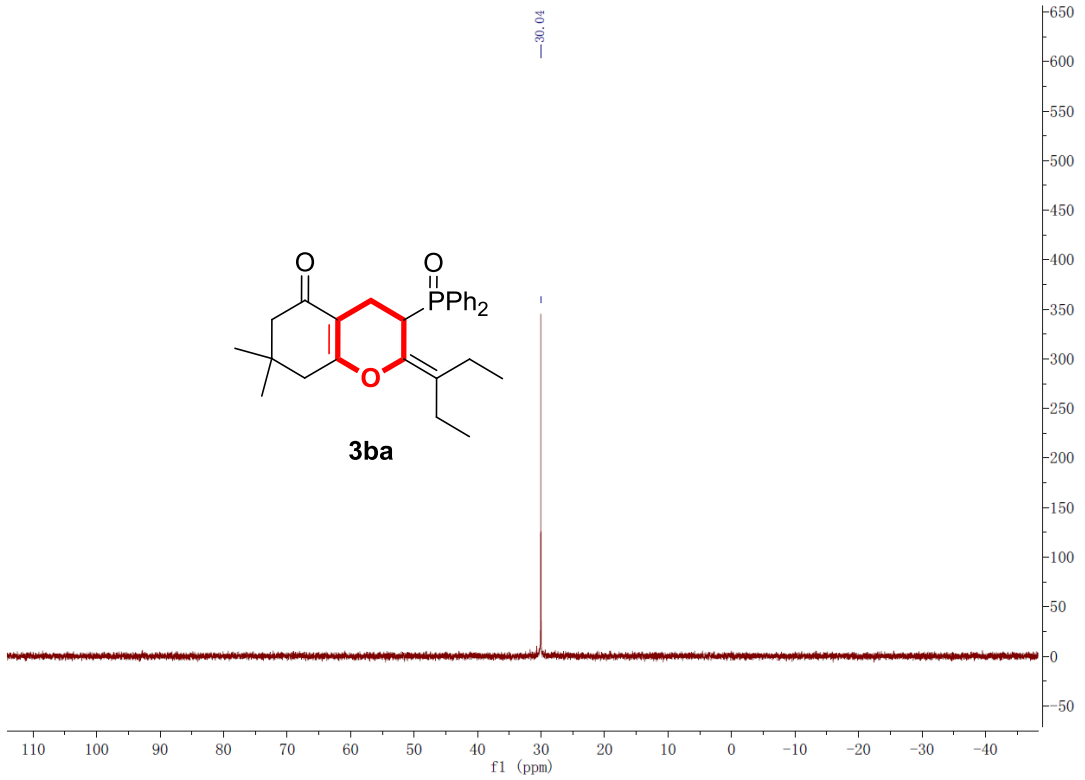
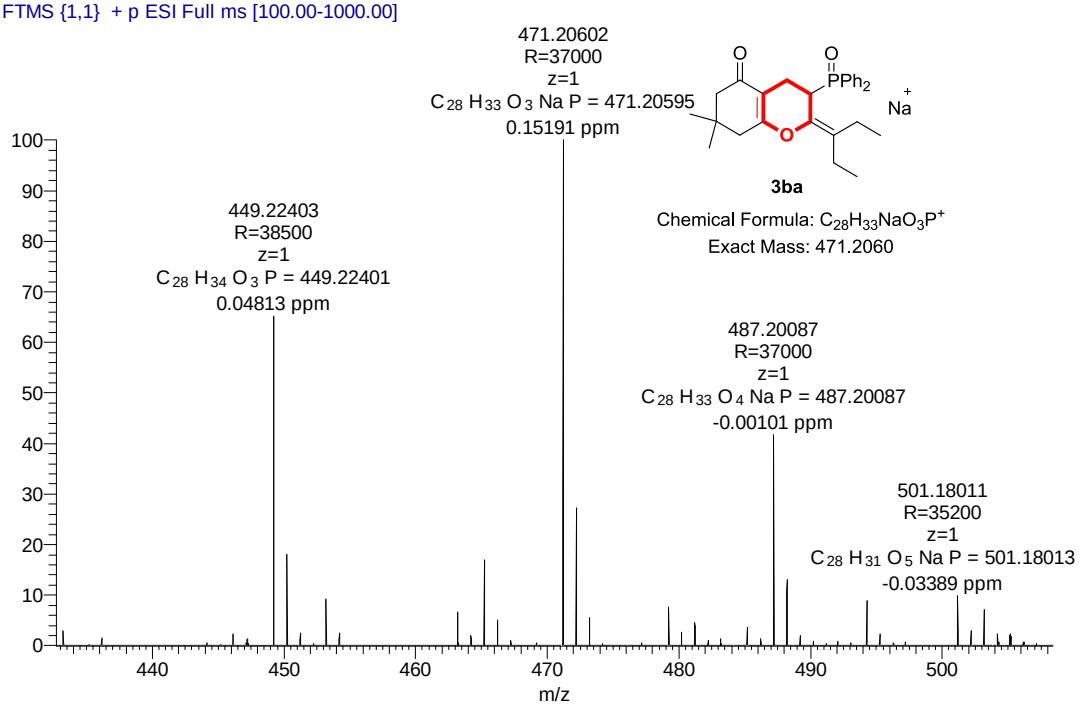
12.36
O
O
PPh2
O
3ba
f1 (ppm)

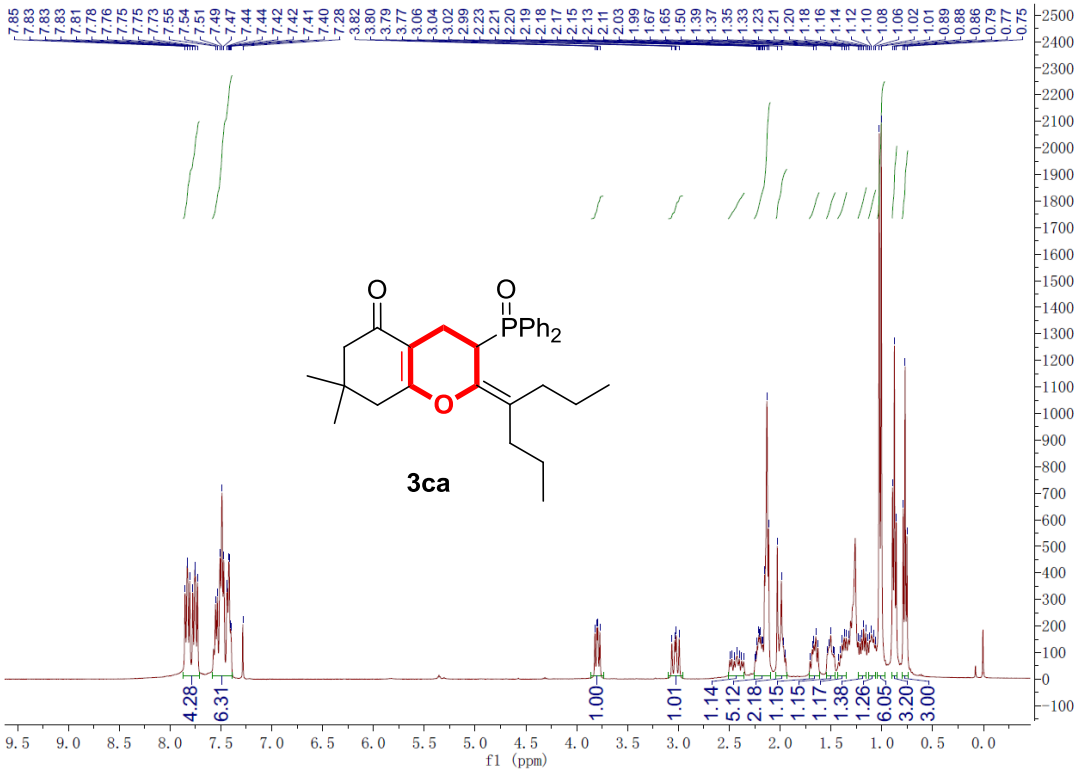

30.04
O
O
PPh2
O
3ba
f1 (ppm)

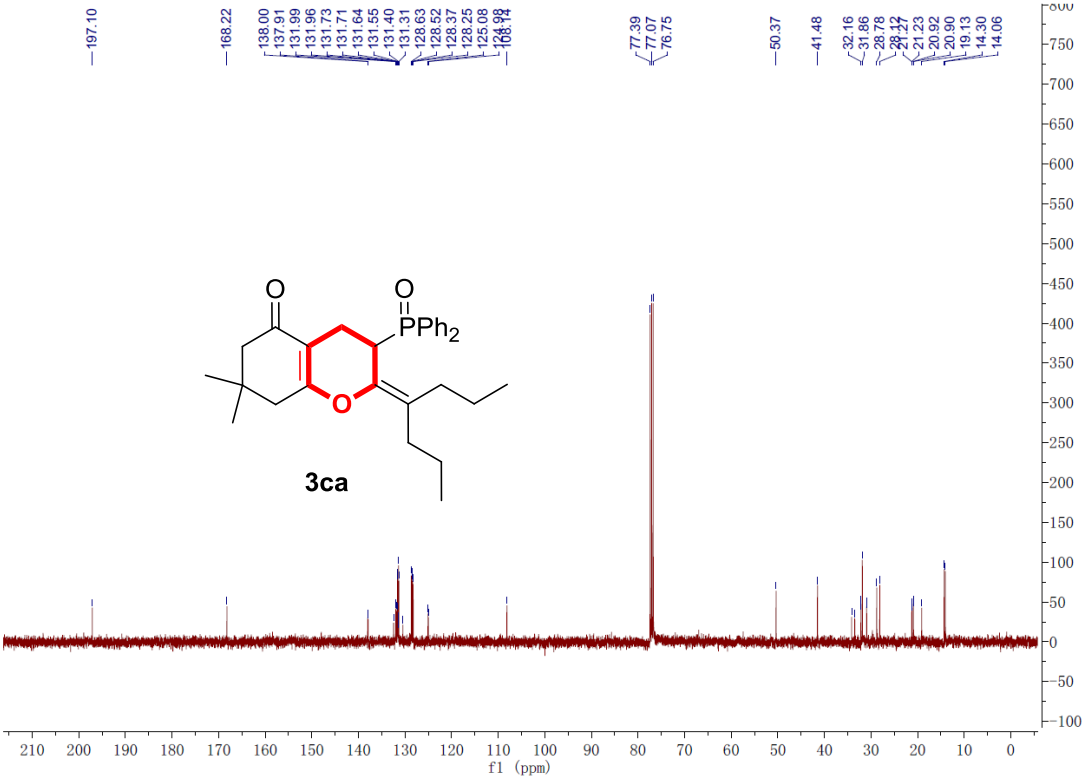
20171124-3 #43 RT: 0.45 AV: 1 NL: 7.17E4
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

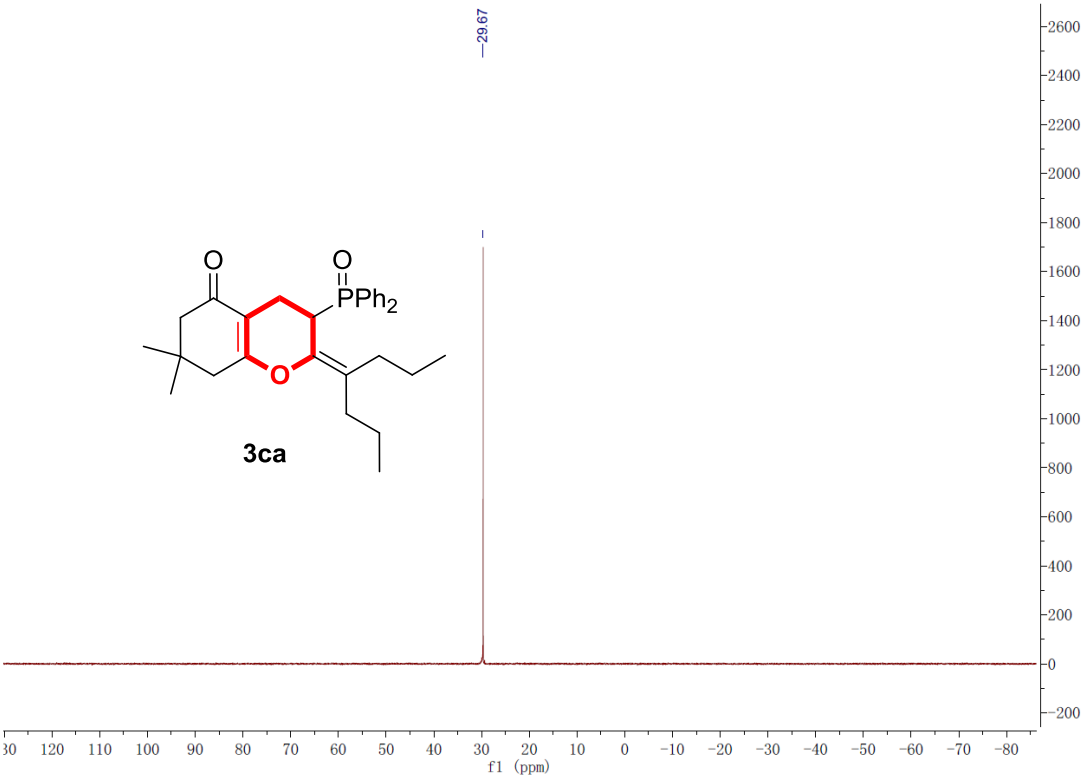




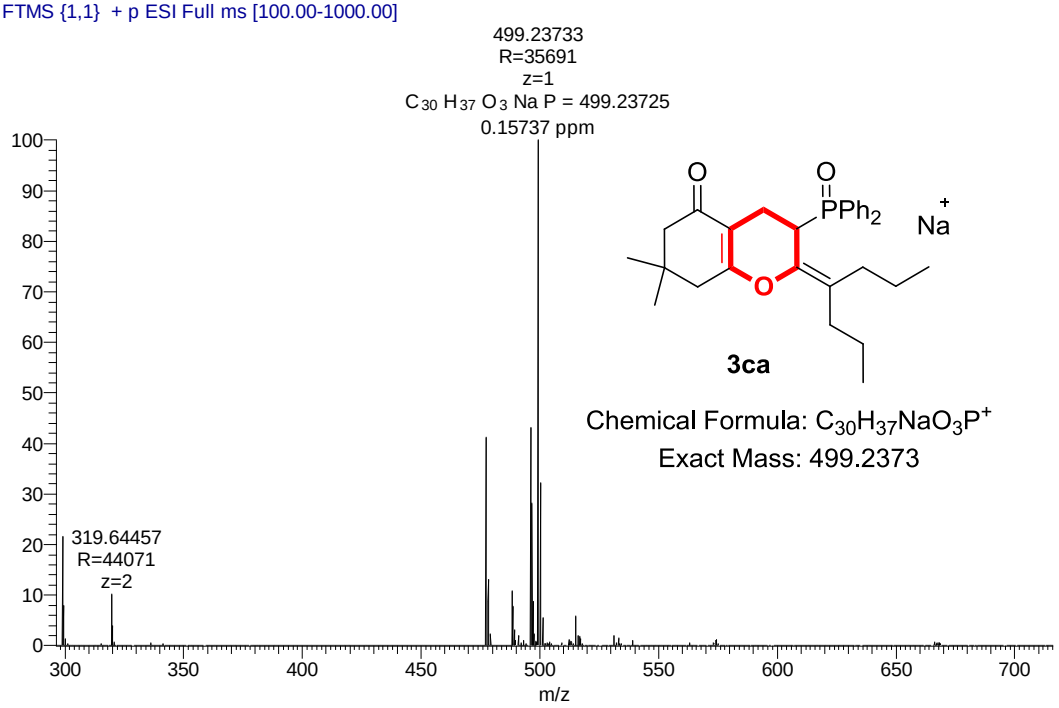


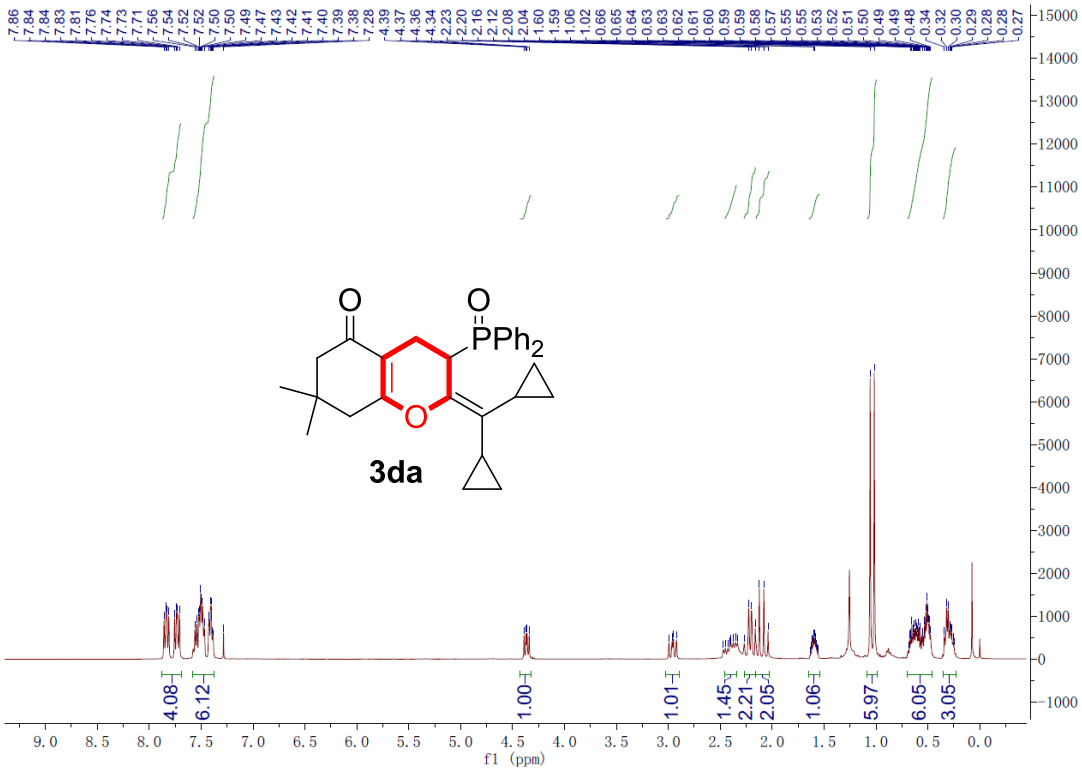


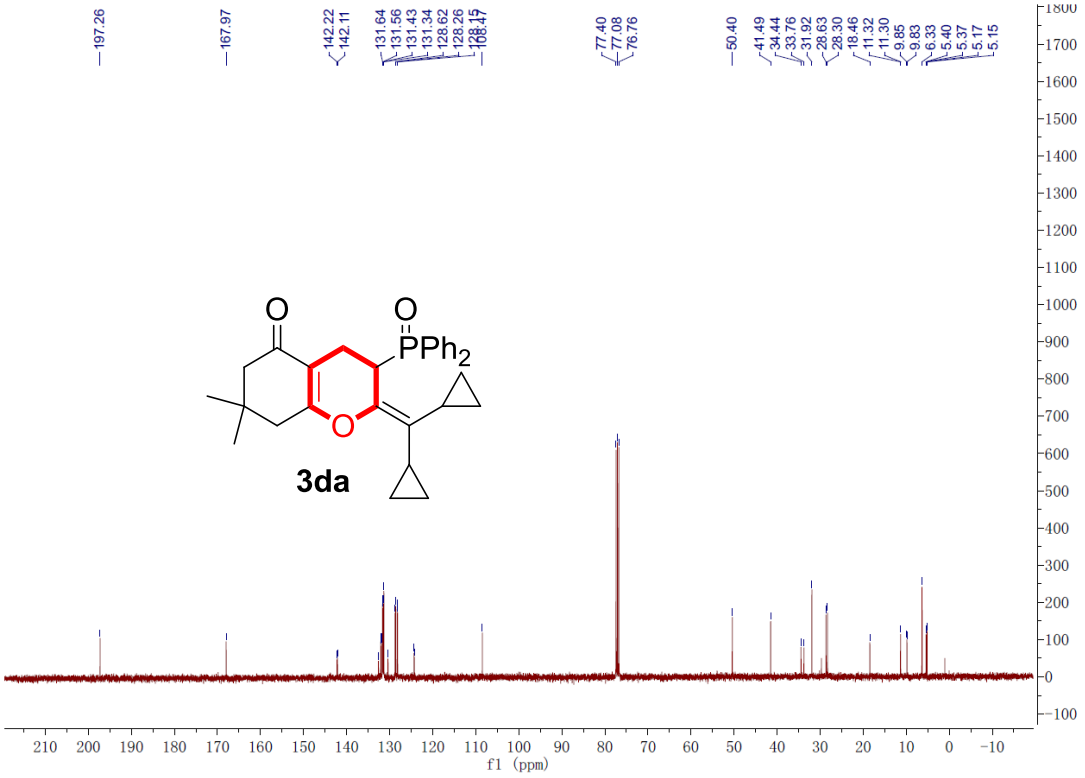

197.10
168.22
138.00
137.91
131.99
131.96
131.73
131.71
131.64
131.55
131.40
131.31
128.63
128.52
128.37
128.25
125.08
77.39
77.07
76.75
50.37
41.48
32.16
31.86
28.78
21.23
20.92
20.90
19.13
14.30
14.06
O
O
PPh2
O
3ca
f1 (ppm)

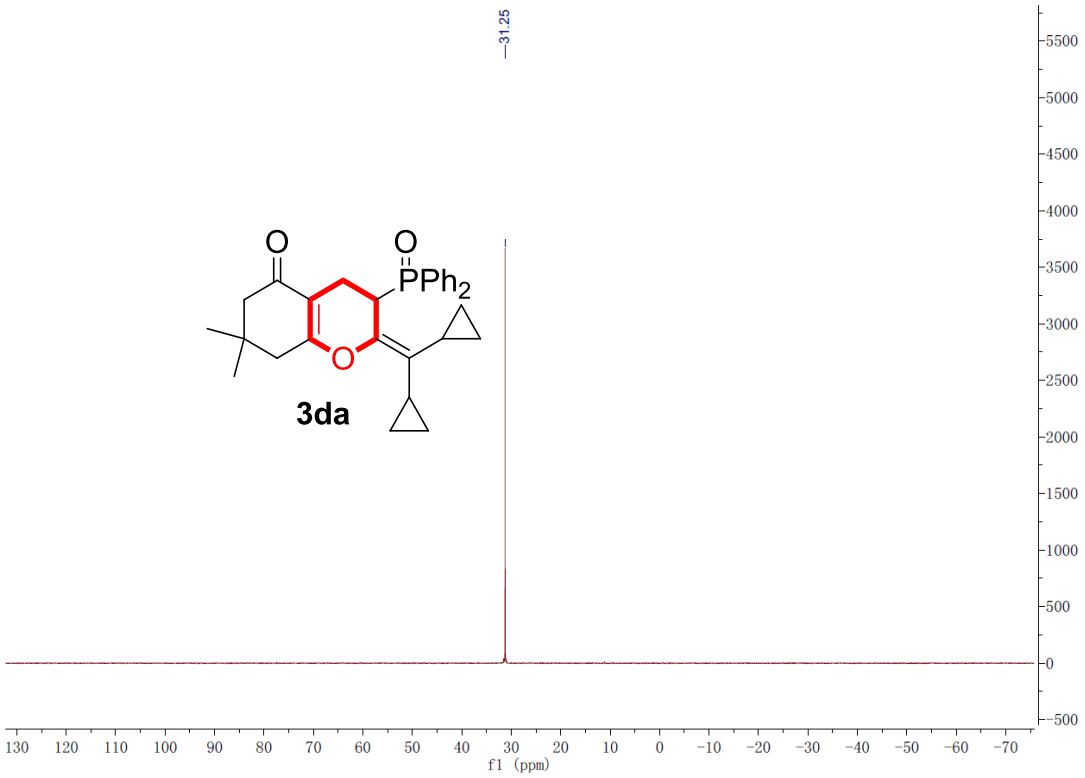

29.67
O
O
PPh2
O
3ca
f1 (ppm)

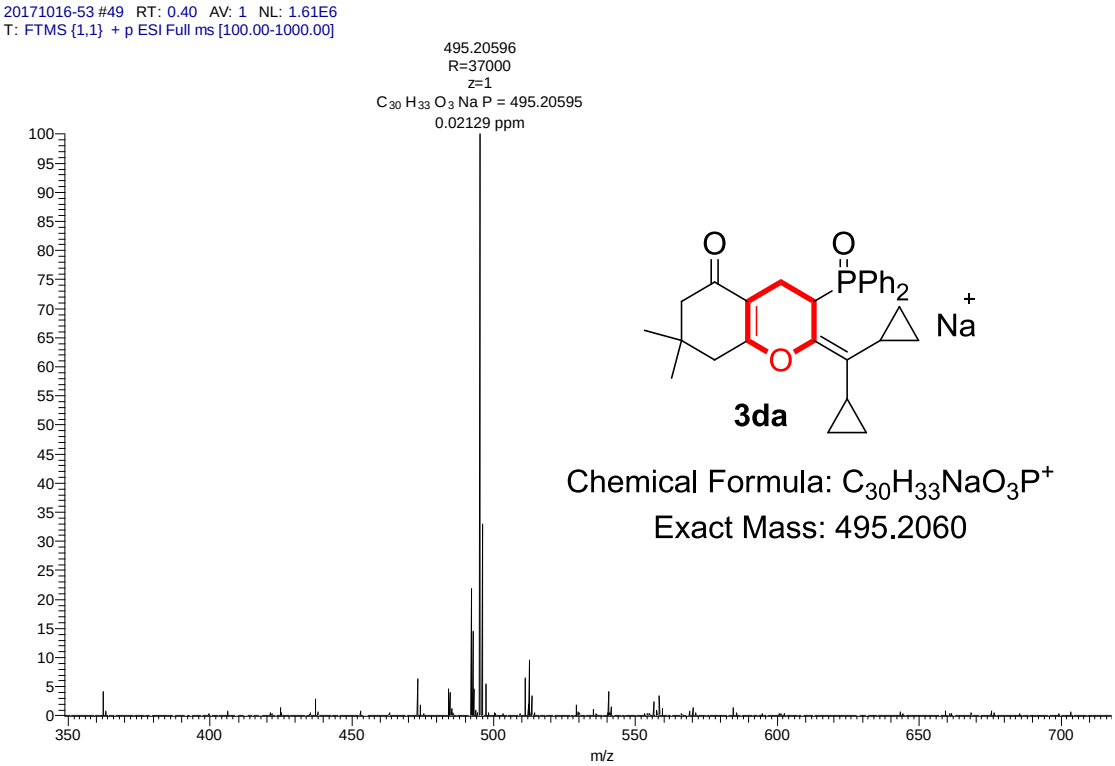
20171124-11 #31-34 RT: 0.27-0.30 AV: 4 NL: 2.83E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

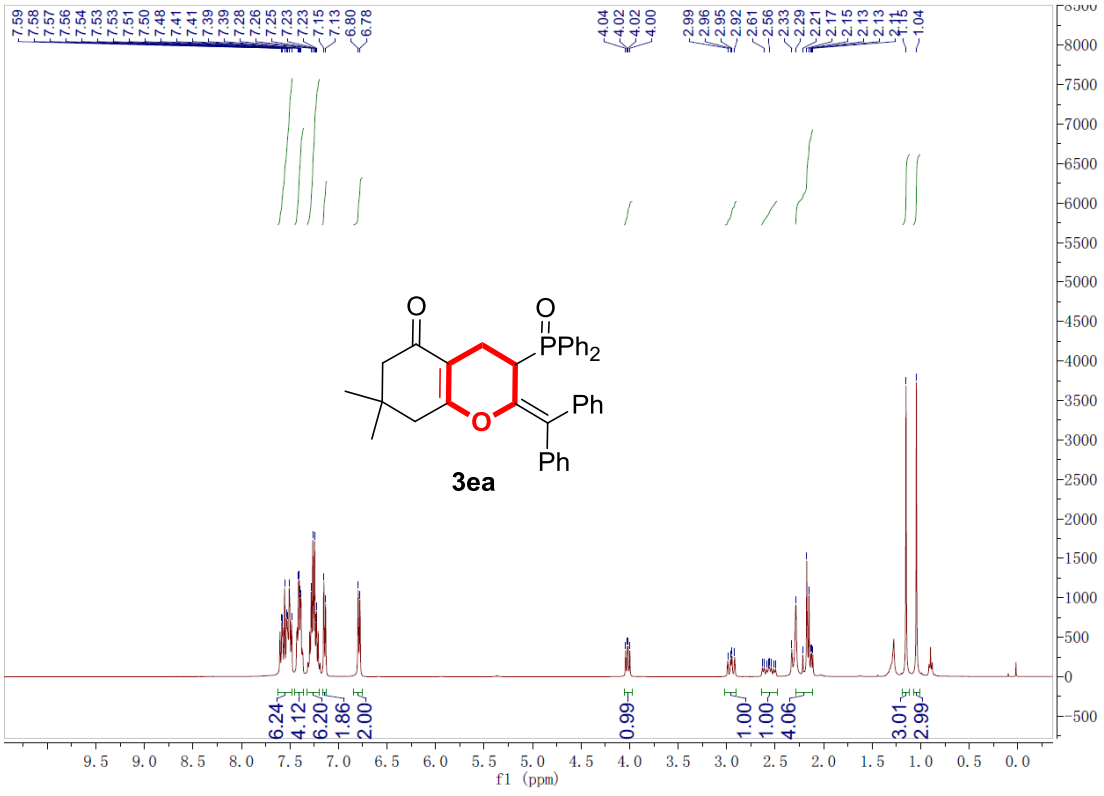


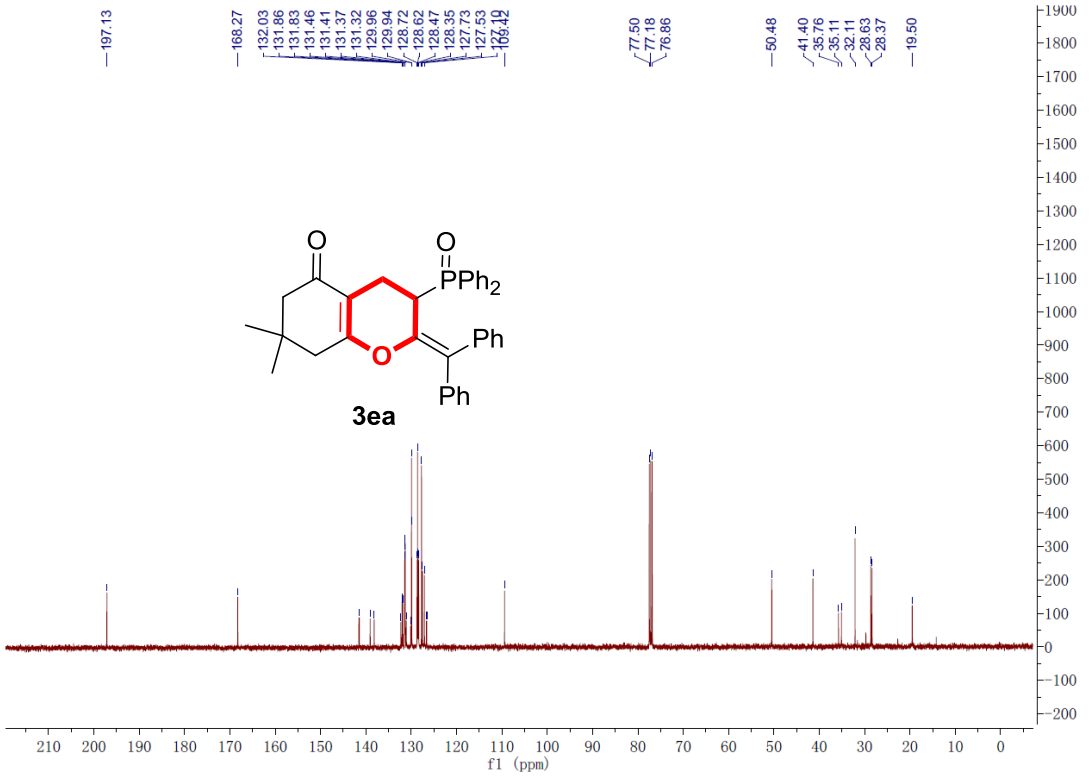



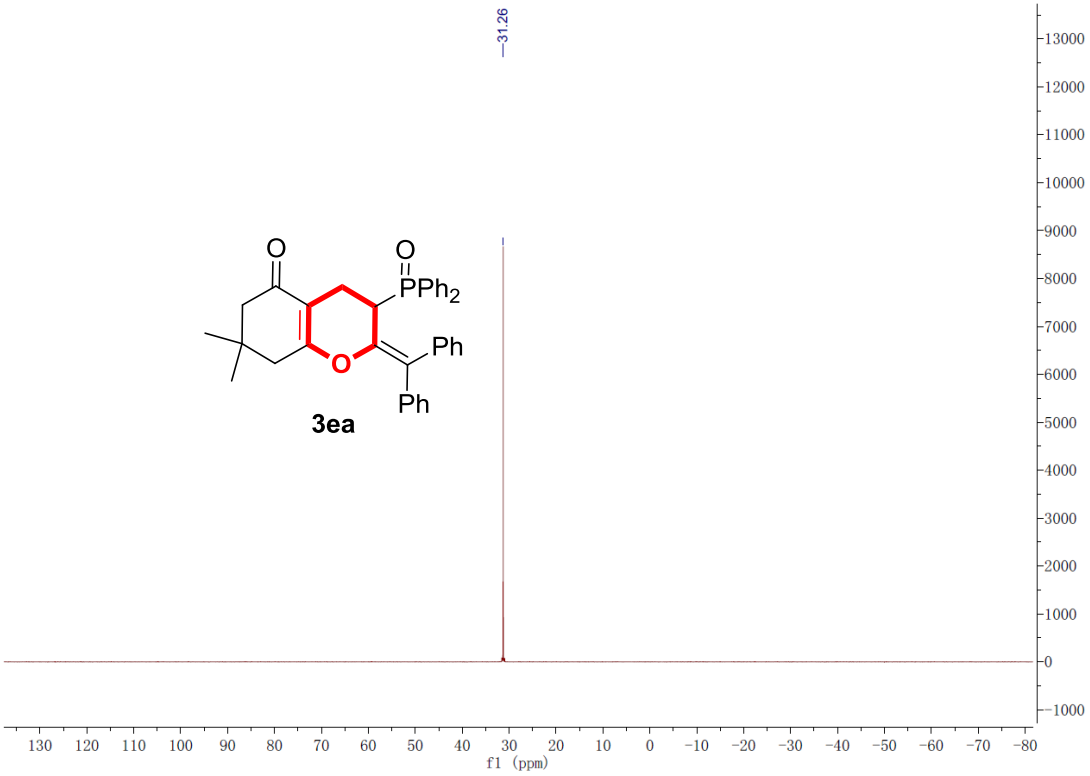

197.26
167.97
142.22
142.11
131.64
131.56
131.43
131.34
128.62
128.26
77.40
77.08
76.76
50.40
41.49
34.44
33.76
31.92
28.63
28.30
18.46
11.32
11.30
9.85
9.83
6.33
5.40
5.37
5.17
5.15
O
O
PPh2
O
3da
f1 (ppm)

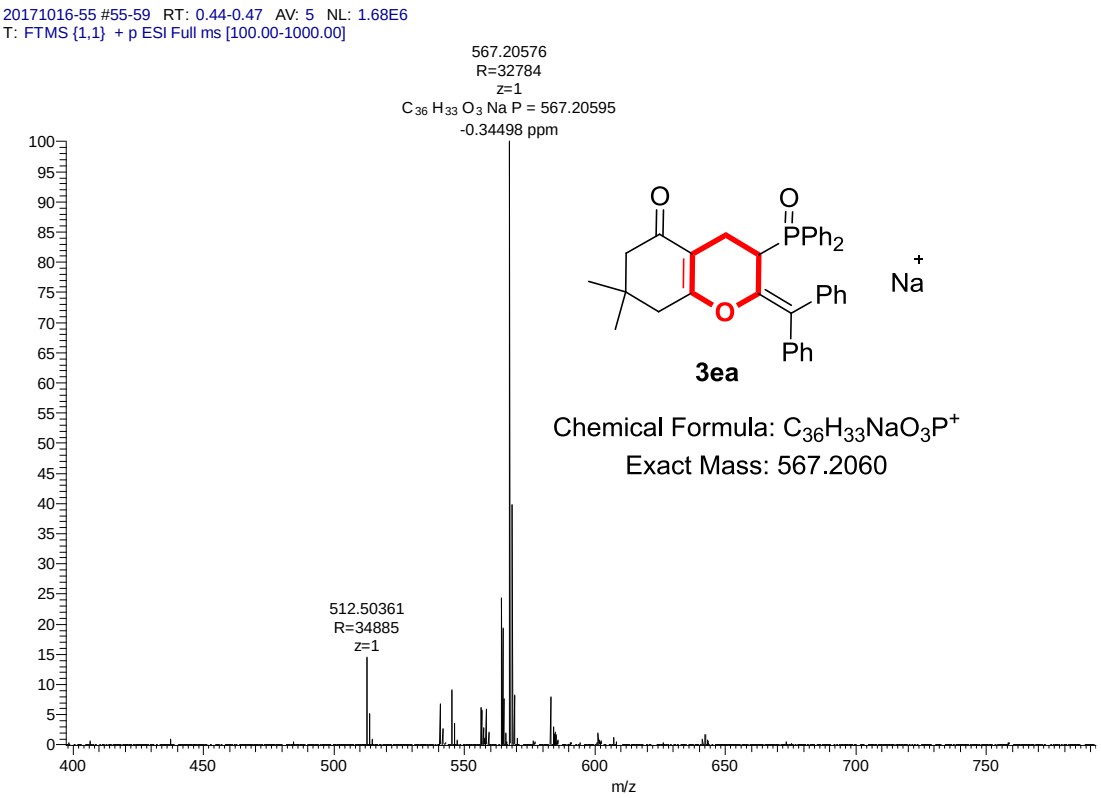

31.25
O
O
PPh2
O
3da
f1 (ppm)

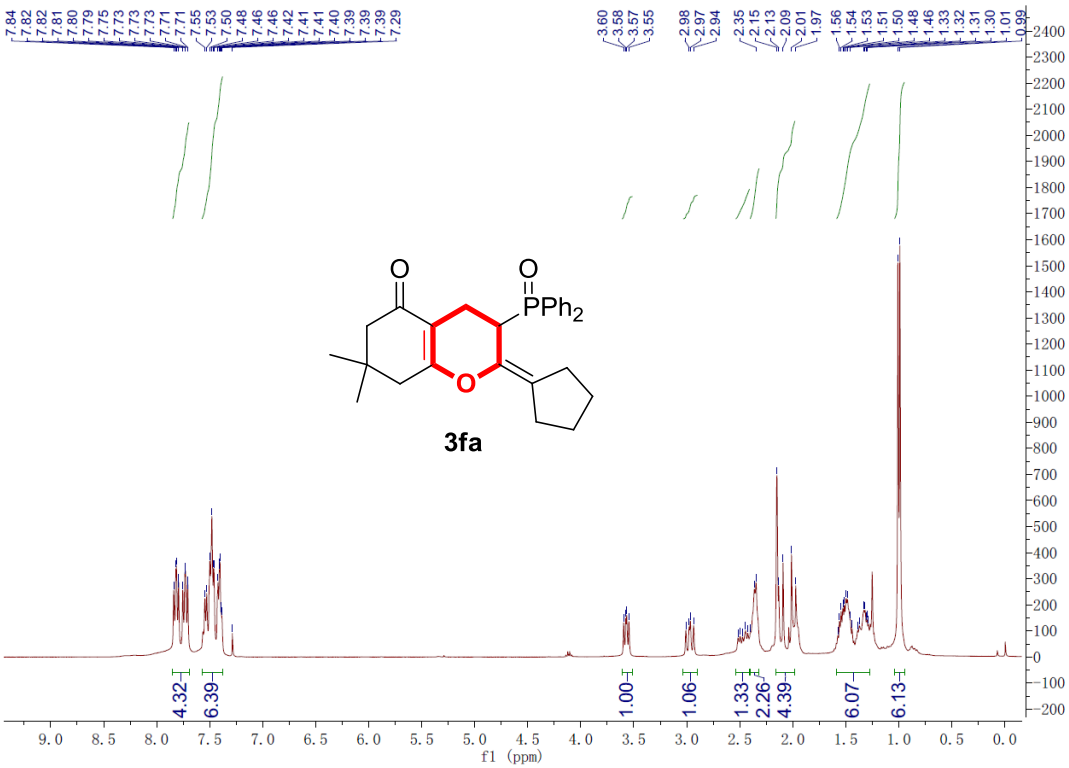

20171016-53 #49 RT: 0.40 AV: 1 NL: 1.61E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
495.20596
R=37000
z=1
C30 H33 O3 Na P = 495.20595
0.02129 ppm
m/z
3da
Chemical Formula: C30H33NaO3P+
Exact Mass: 495.2060

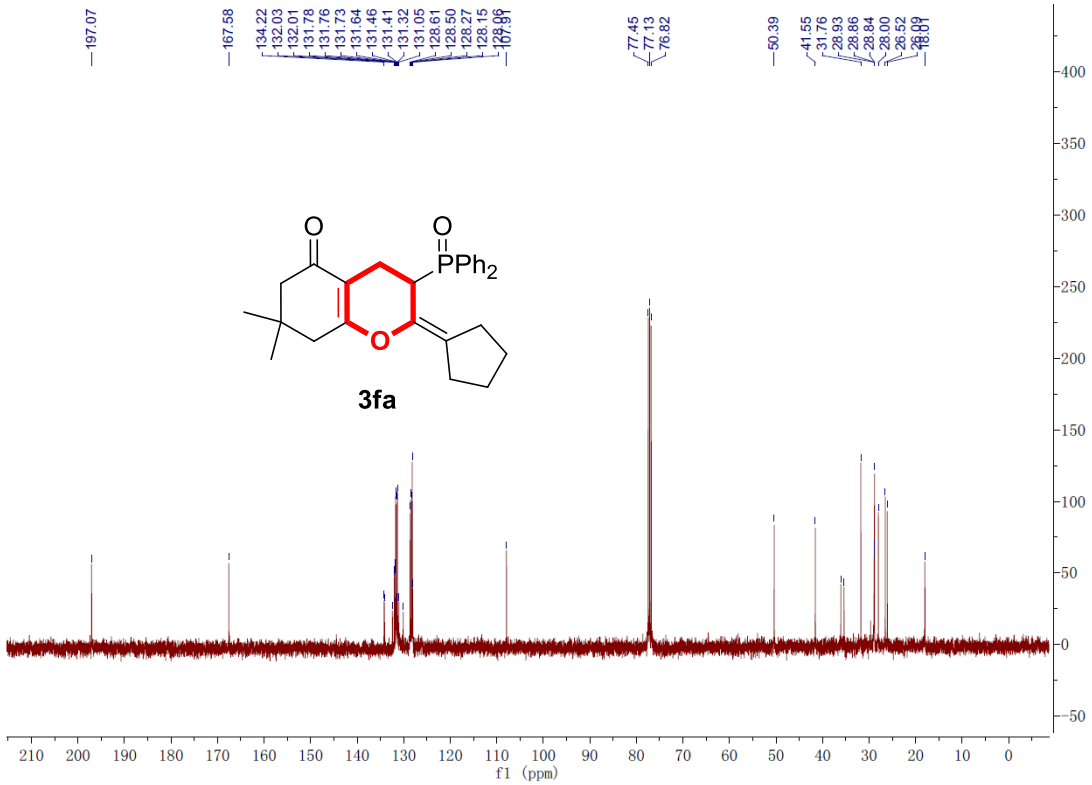

3ea
f1 (ppm)

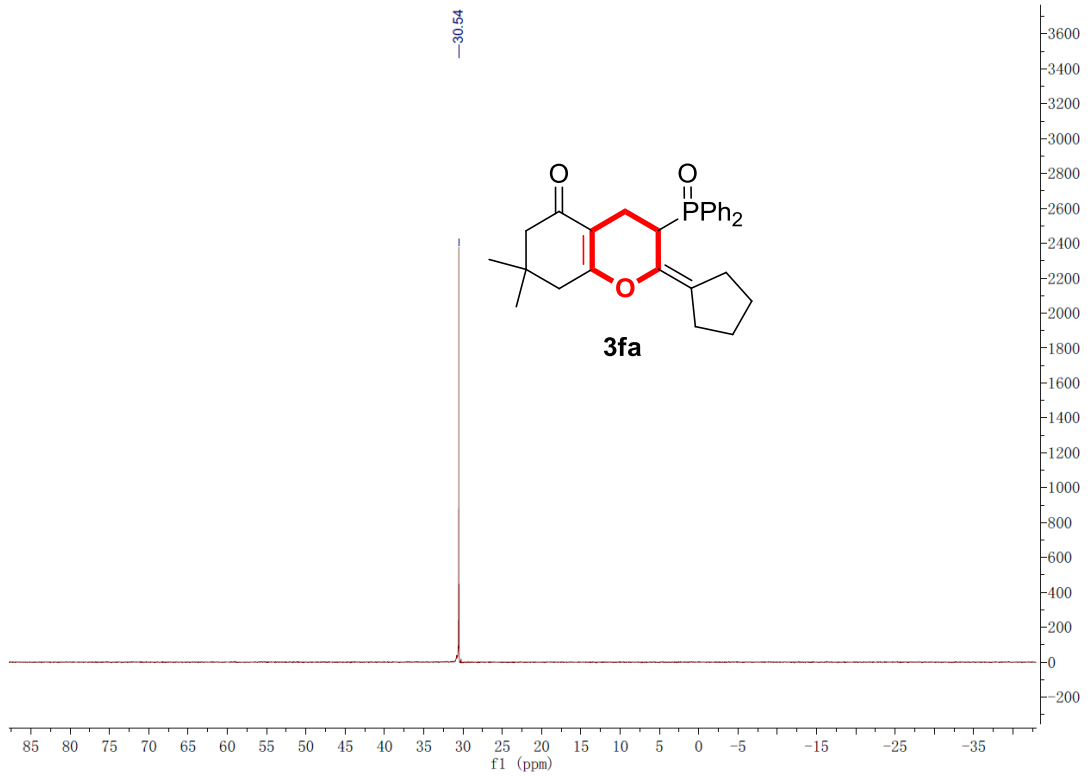

197.13
168.27
132.03
131.86
131.83
131.46
131.41
131.37
131.32
129.96
129.94
128.72
128.62
128.47
128.35
127.73
127.53
77.50
77.18
76.86
60.48
41.40
35.76
35.11
32.11
28.63
28.37
19.50
O
O
PPh2
Ph
O
Ph
3ea
f1 (ppm)

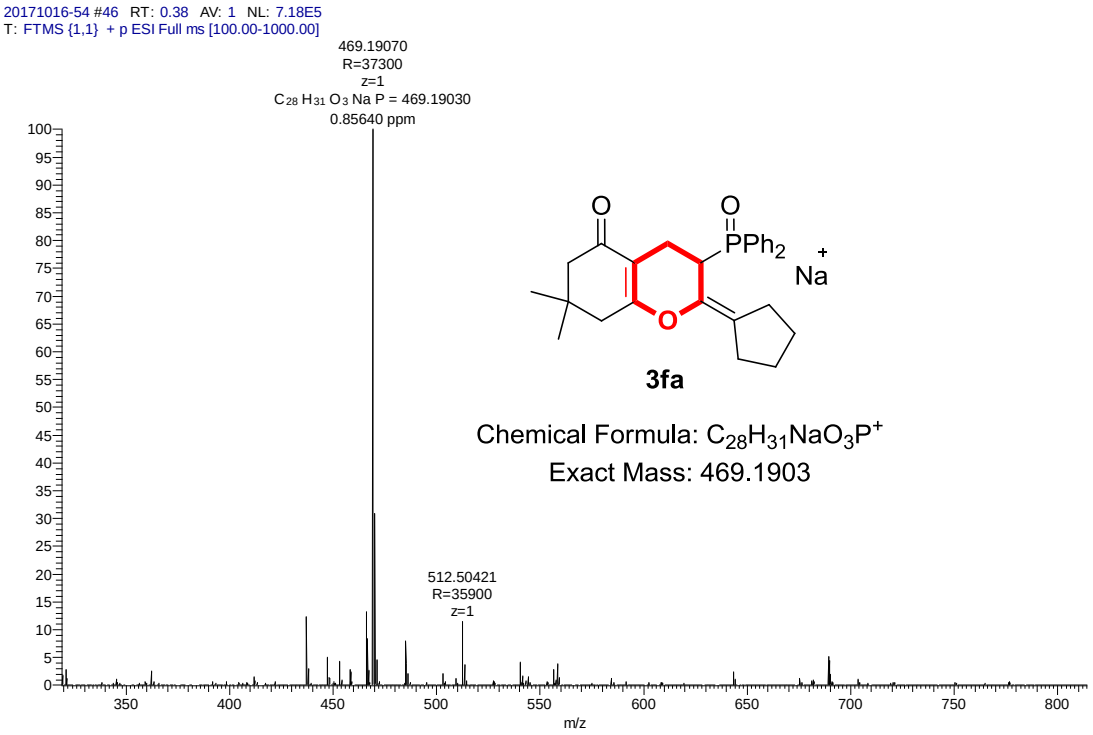

31.26
O
O
PPh2
Ph
O
Ph
3ea
f1 (ppm)

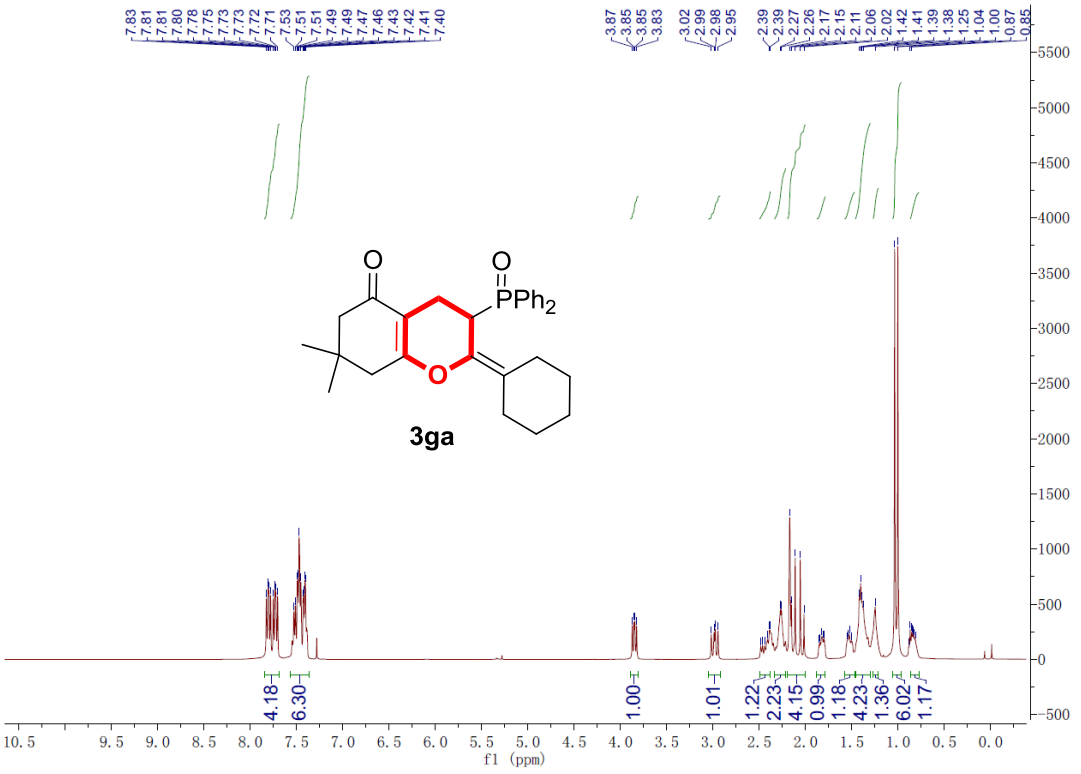

20171016-55 #55-59 RT: 0.44-0.47 AV: 5 NL: 1.68E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
567.20576
R=32784
z=1
C36 H33 O3 Na P = 567.20595
-0.34498 ppm
512.50361
R=34885
z=1
m/z
3ea
Chemical Formula: C36H33NaO3P+
Exact Mass: 567.2060

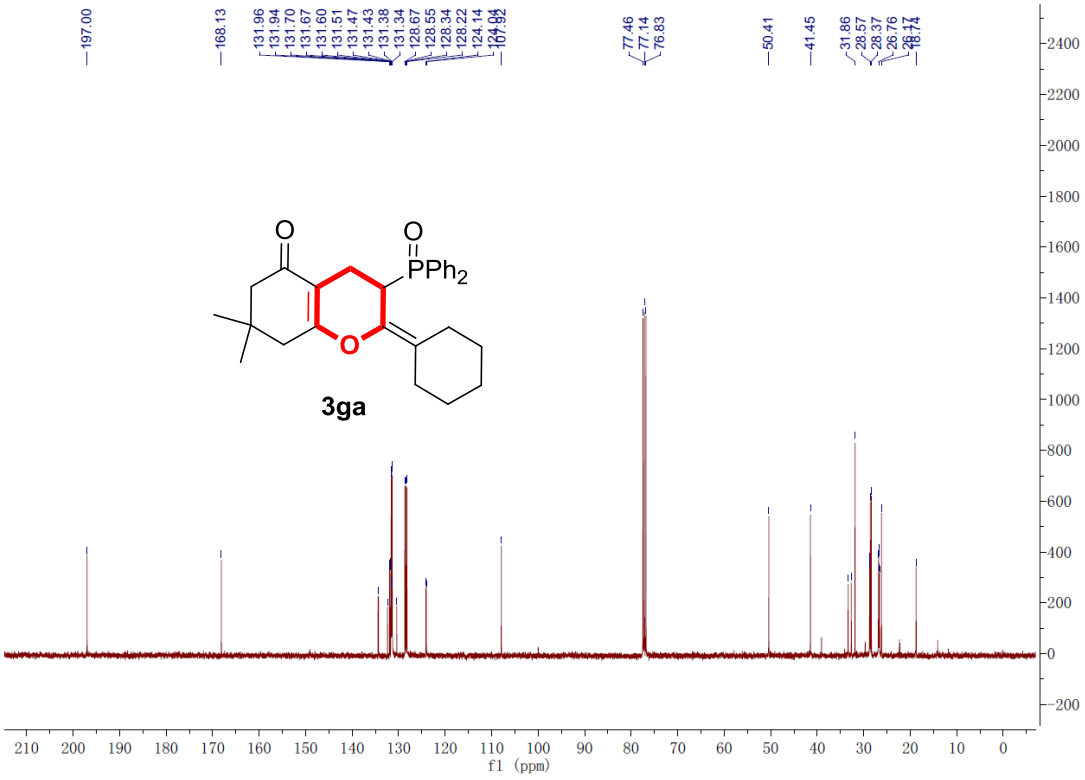

3fa
f1 (ppm)

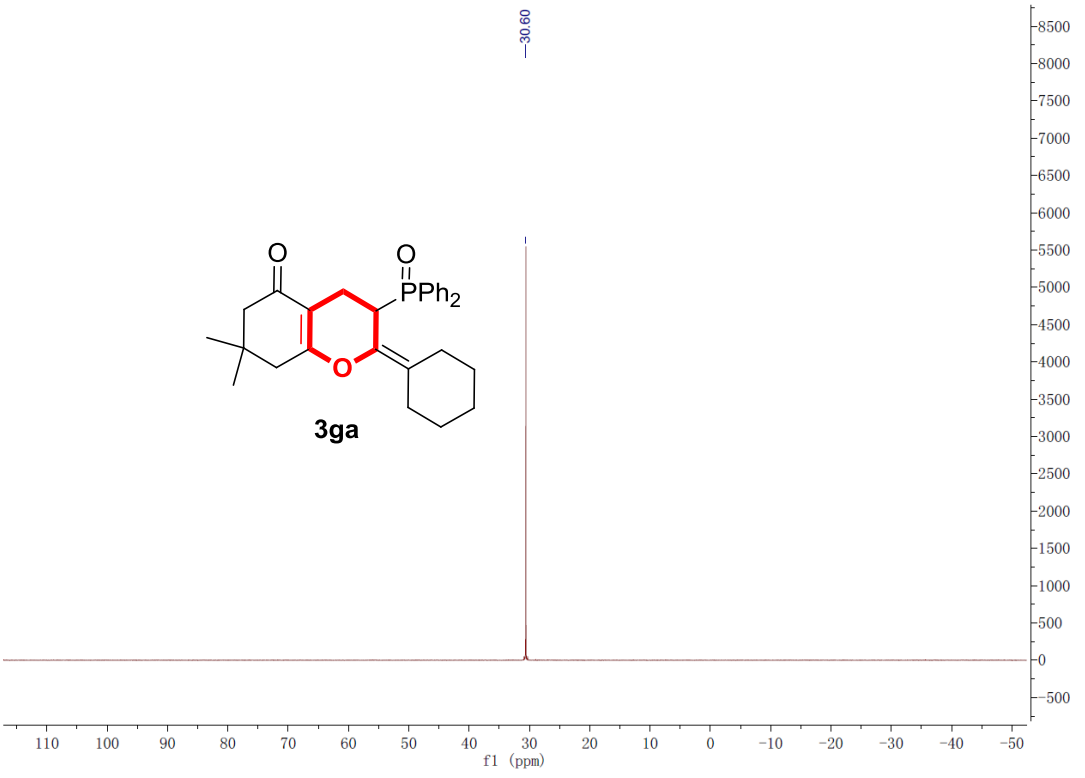

197.07
167.58
134.22
132.03
132.01
131.78
131.76
131.73
131.64
131.46
131.41
131.32
131.05
128.61
128.50
128.27
128.15
77.45
77.13
76.82
50.39
41.55
31.76
28.93
28.86
28.84
28.00
26.52
O
O
PPh2
O
3fa
f1 (ppm)


30.54
O
O
PPh2
O
3fa
f1 (ppm)

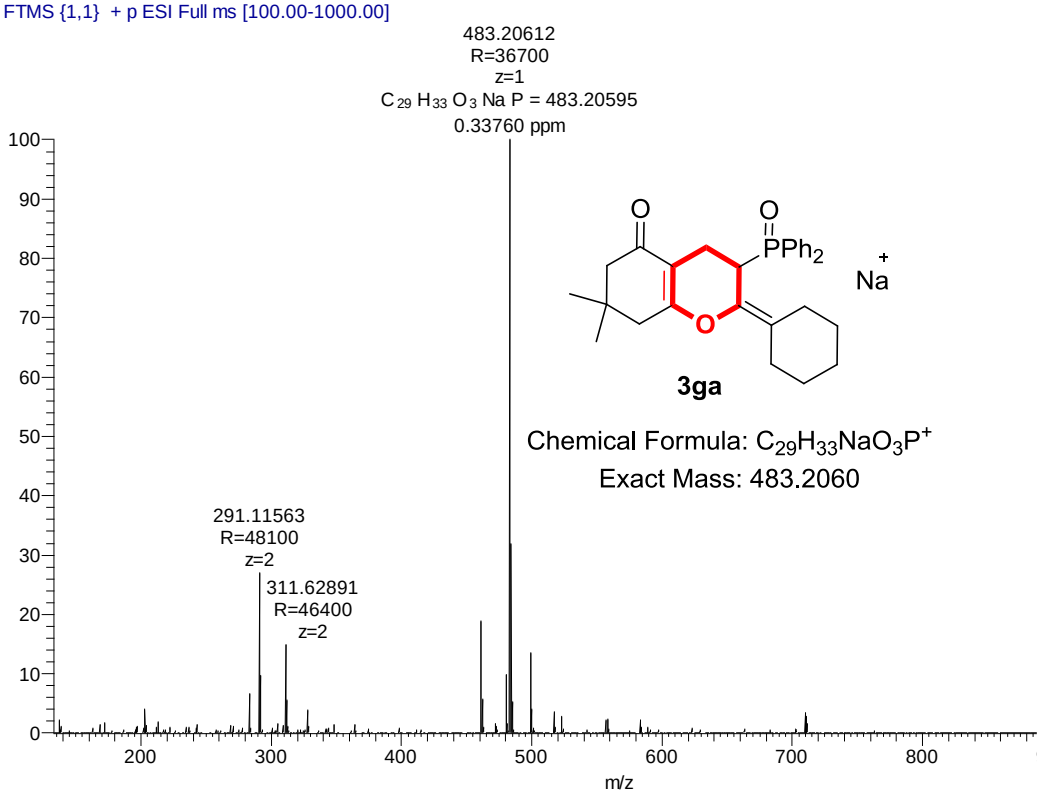

20171016-54 #46 RT: 0.38 AV: 1 NL: 7.18E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
469.19070
R=37300
z=1
C28 H31 O3 Na P = 469.19030
0.85640 ppm
512.50421
R=35900
z=1
m/z
3fa
Chemical Formula: C28H31NaO3P+
Exact Mass: 469.1903

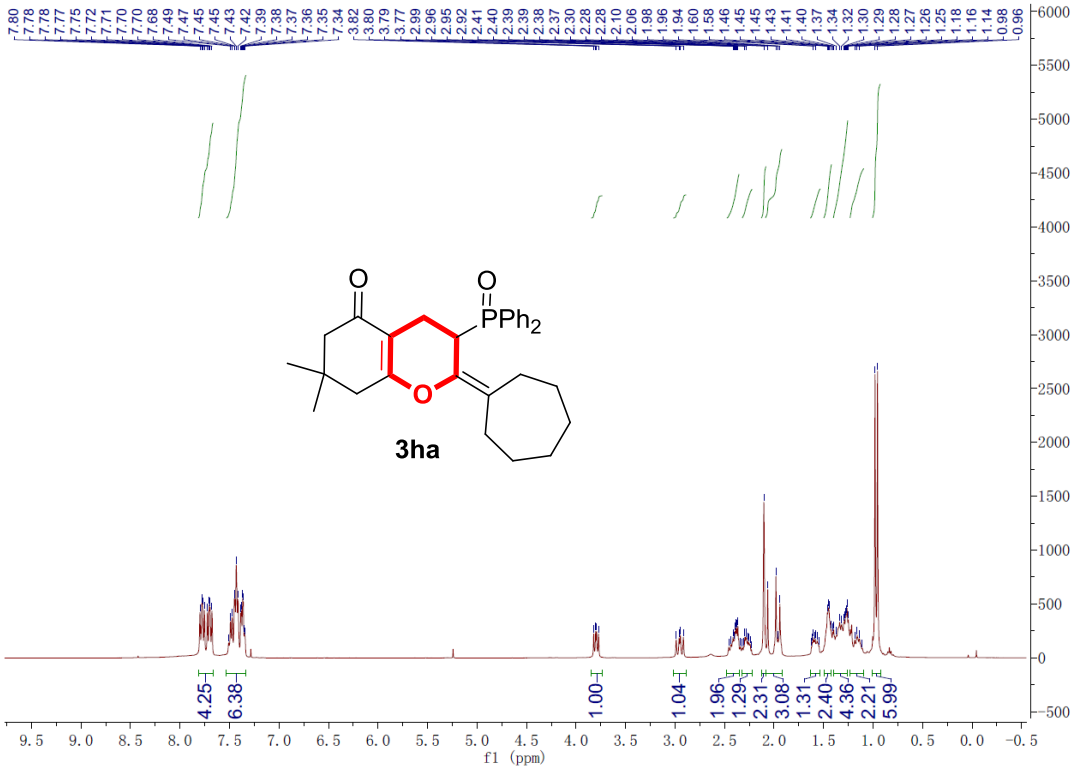

3ga
f1 (ppm)

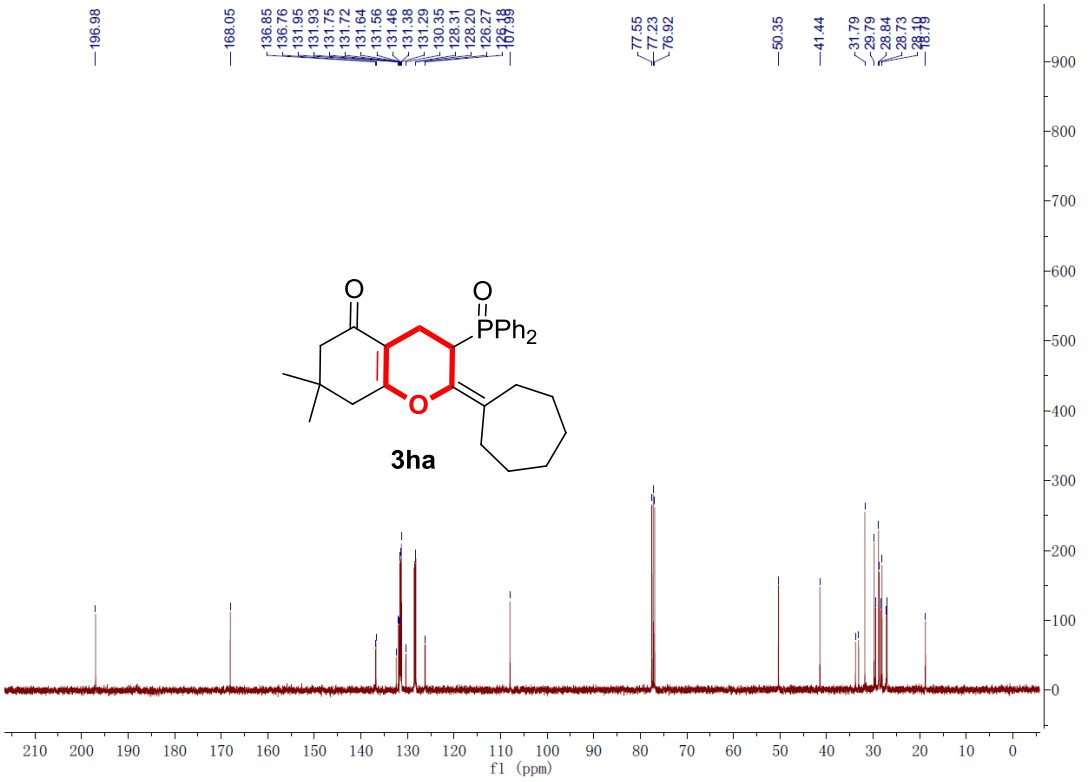

197.00
168.13
131.96
131.94
131.70
131.67
131.60
131.51
131.47
131.43
131.38
131.34
128.67
128.55
128.34
128.22
124.14
77.46
77.14
76.83
50.41
41.45
31.86
28.57
28.37
26.76
O
O
PPh2
O
3ga
f1 (ppm)

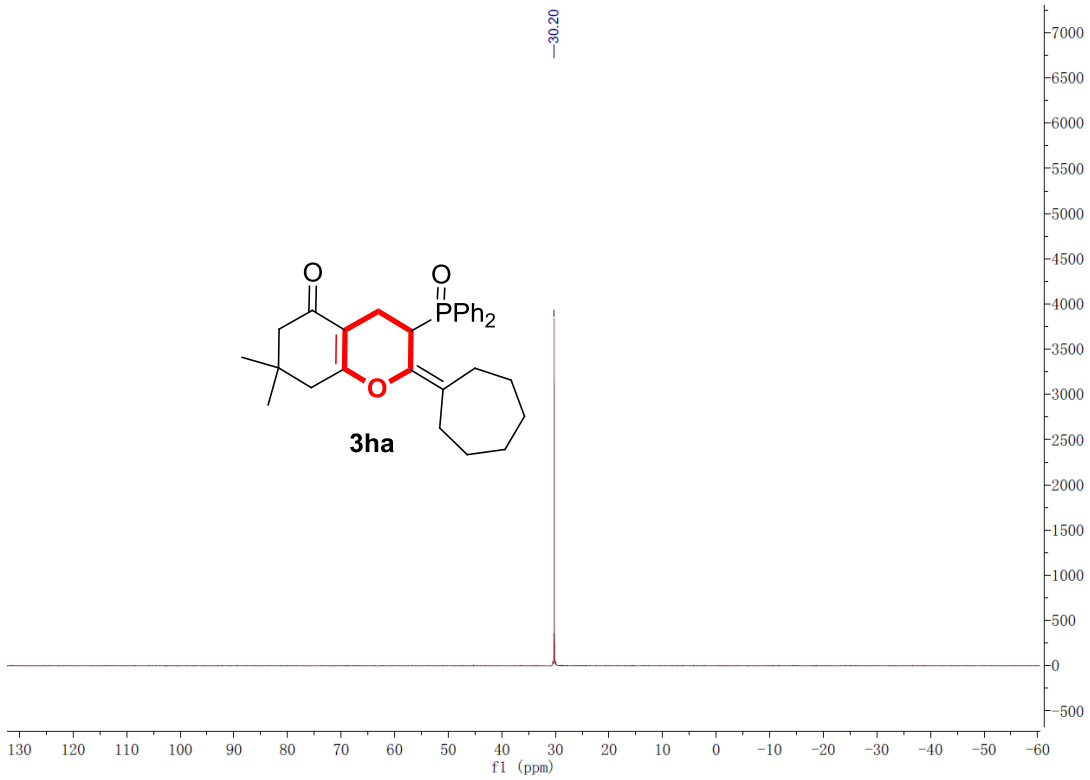

30.60
O
O
PPh2
O
3ga
f1 (ppm)

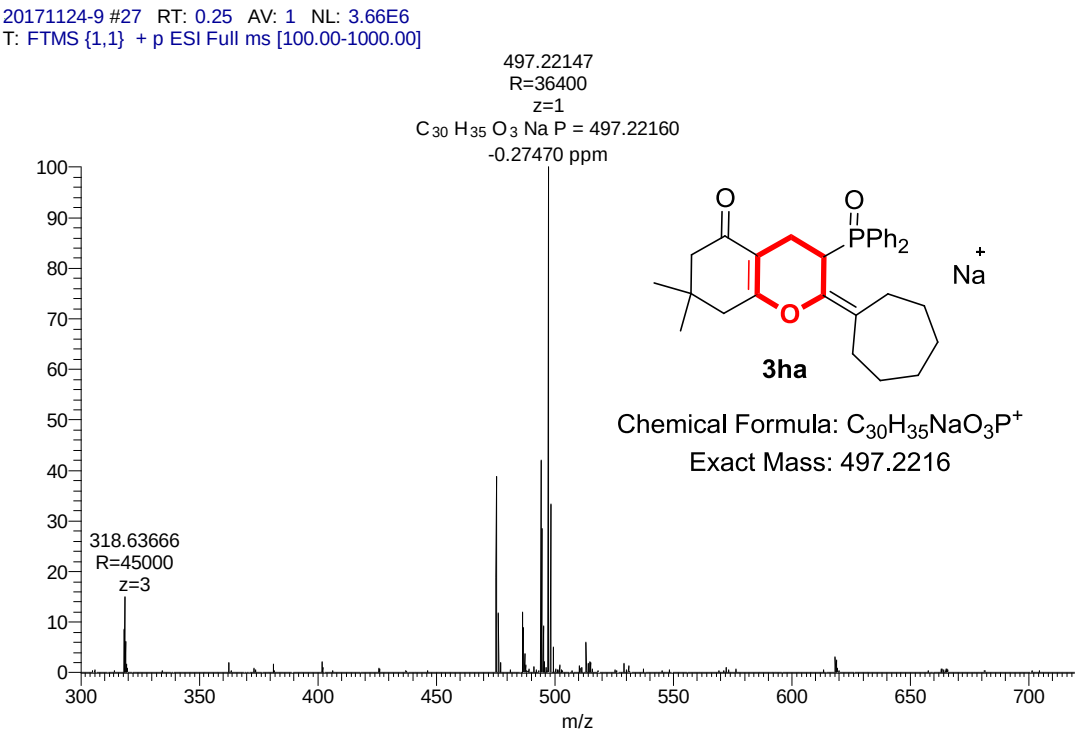
20180104-37 #31 RT: 0.46 AV: 1 NL: 6.09E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

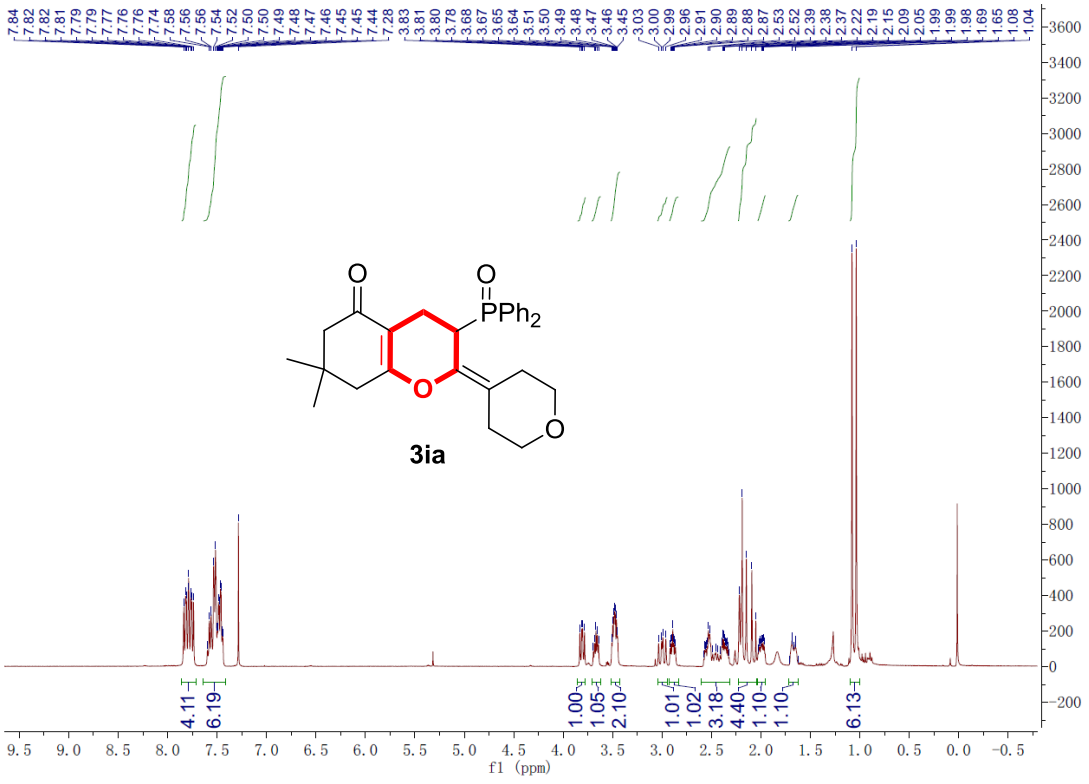


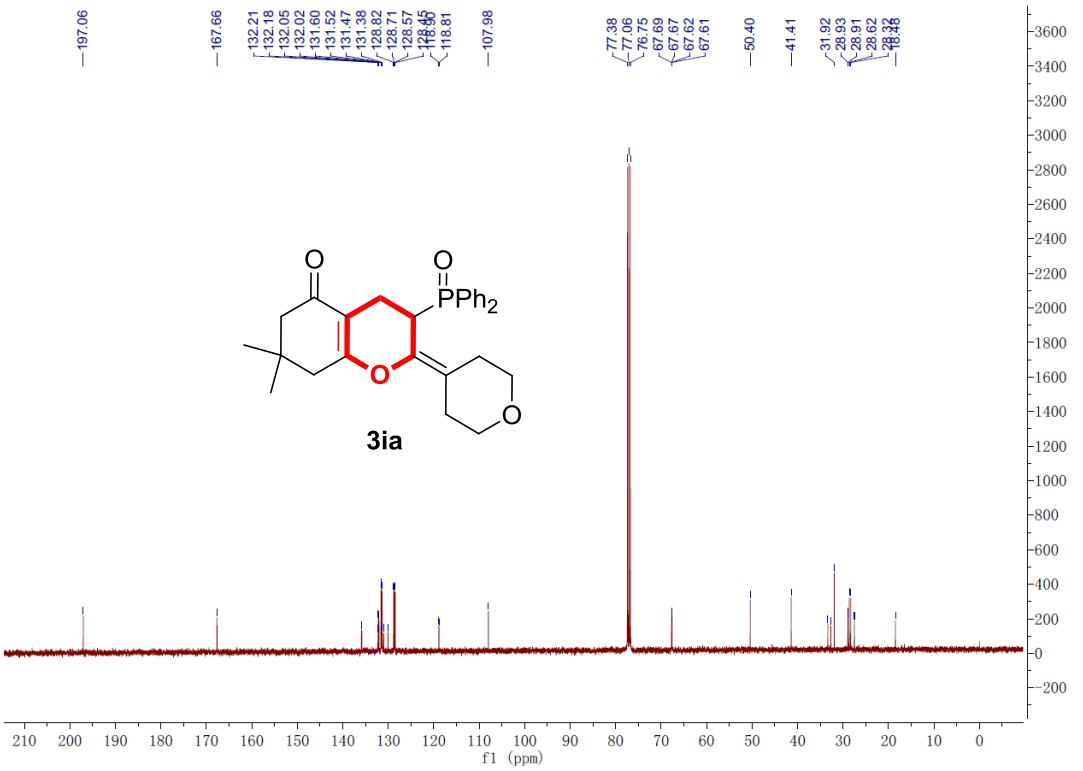



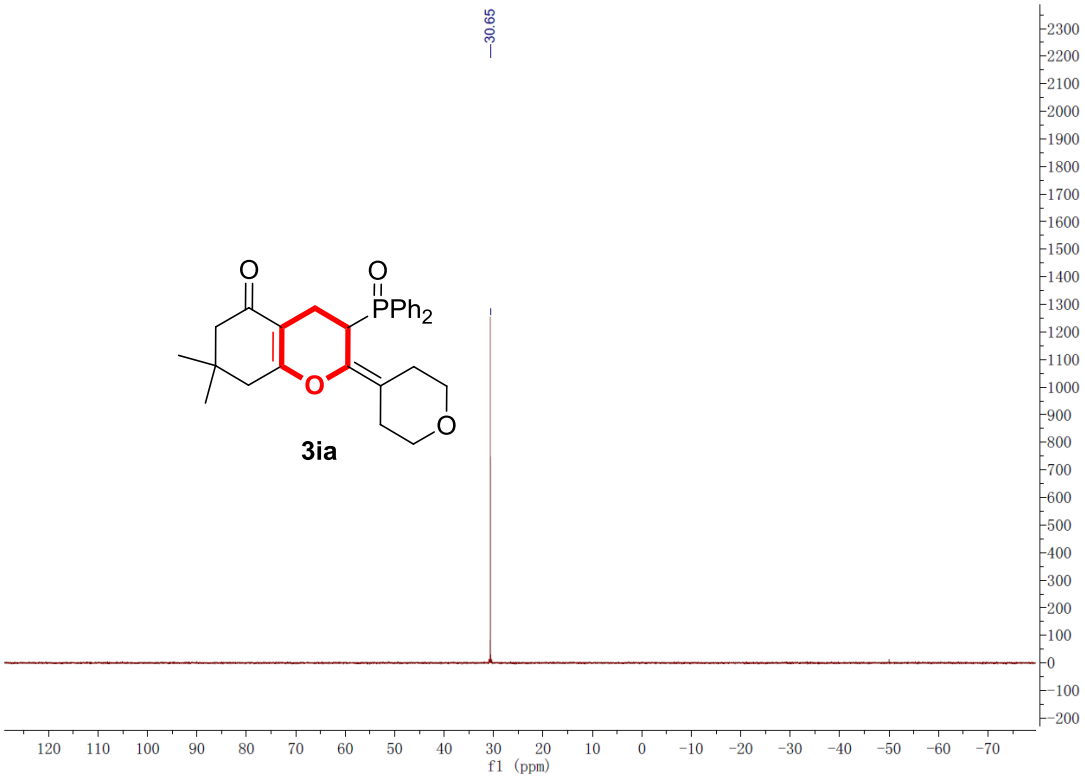

196.98
168.05
136.85
136.76
131.95
131.93
131.75
131.72
131.64
131.56
131.46
131.38
131.29
130.35
128.31
128.20
126.27
107.99
77.55
77.23
76.92
50.35
41.44
31.79
29.79
28.84
28.73
O
O
PPh2
O
3ha
f1 (ppm)


30.20
O
O
PPh2
O
3ha
f1 (ppm)

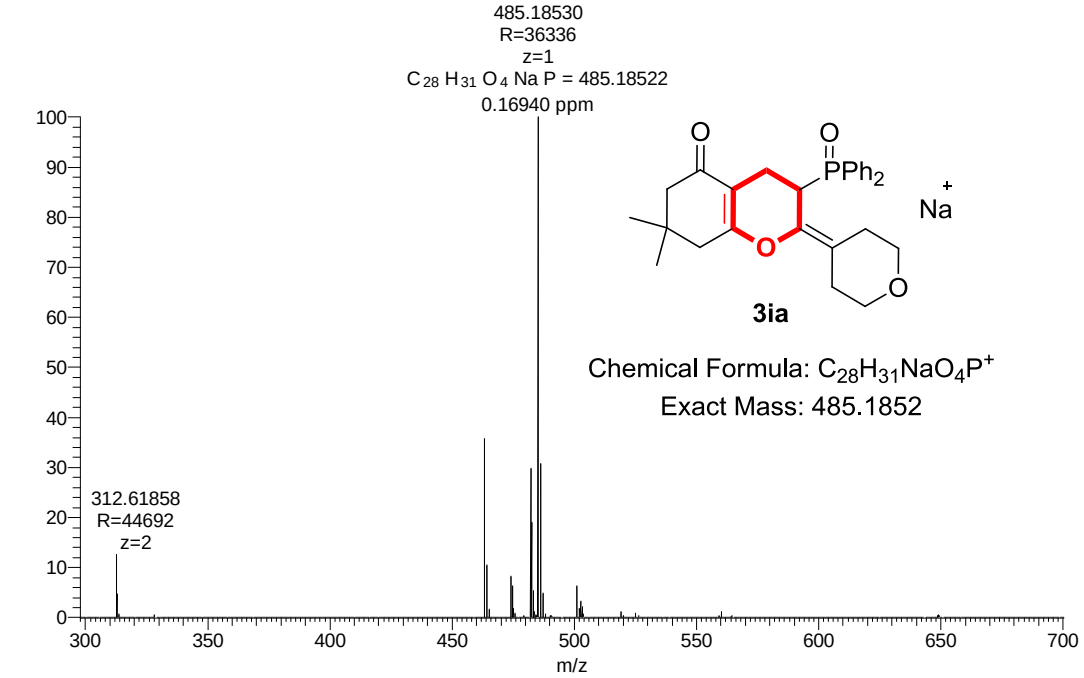

20171124-9 #27 RT: 0.25 AV: 1 NL: 3.66E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
497.22147
R=36400
z=1
C30 H35 O3 Na P = 497.22160
-0.27470 ppm
318.63666
R=45000
z=3
m/z
3ha
Chemical Formula: C30H35NaO3P+
Exact Mass: 497.2216

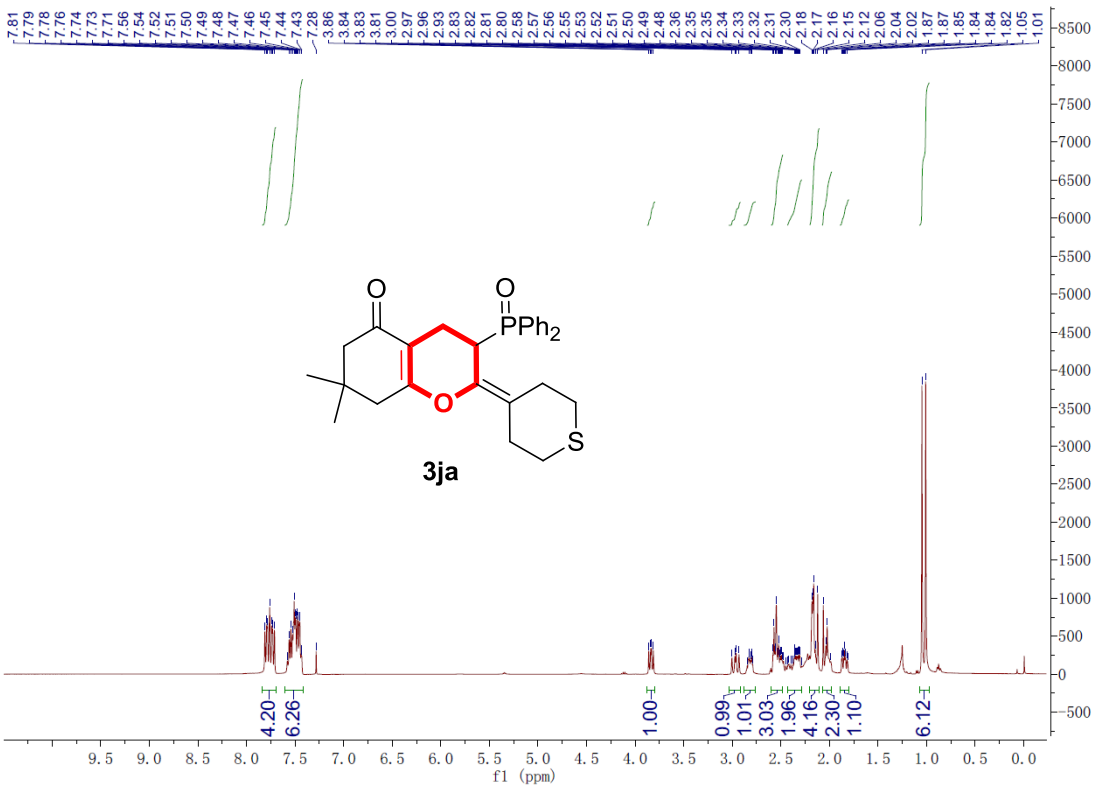

3ia
f1 (ppm)

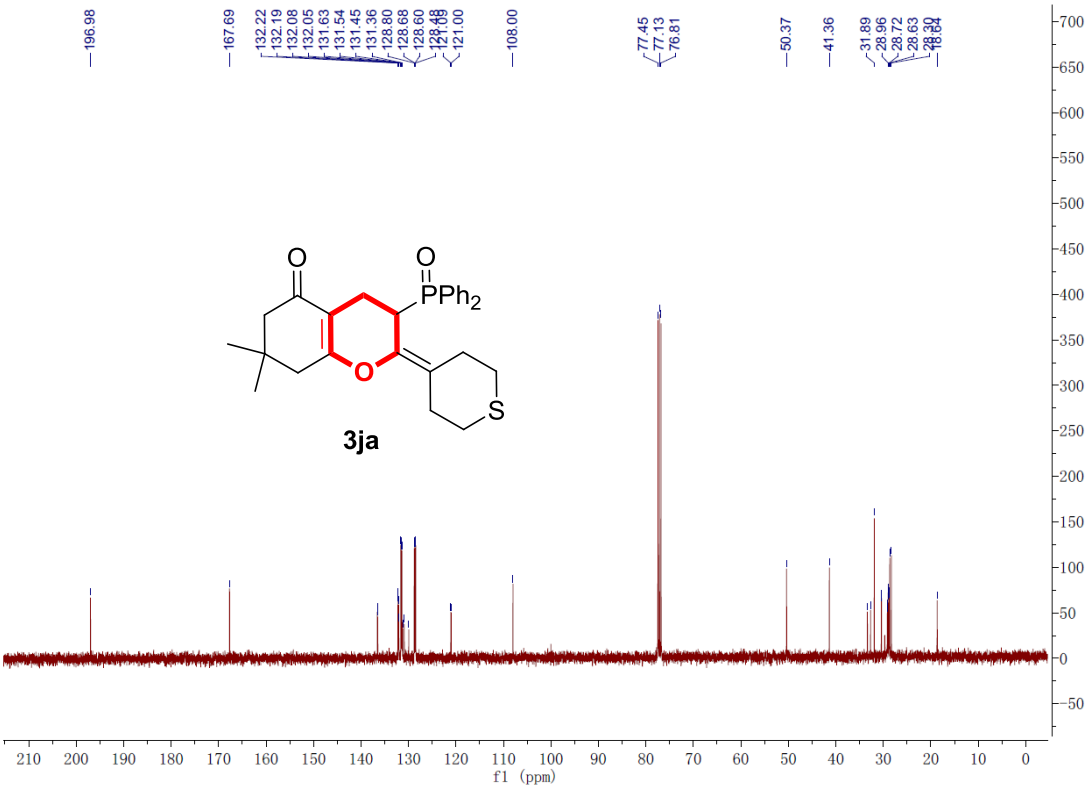

197.06
167.66
132.21
132.18
132.05
132.02
131.60
131.52
131.47
131.38
128.82
128.71
128.57
118.81
107.98
77.38
77.06
76.75
67.69
67.67
67.62
67.61
50.40
41.41
31.92
28.93
28.91
28.62
O
O
PPh2
O
O
3ia
f1 (ppm)

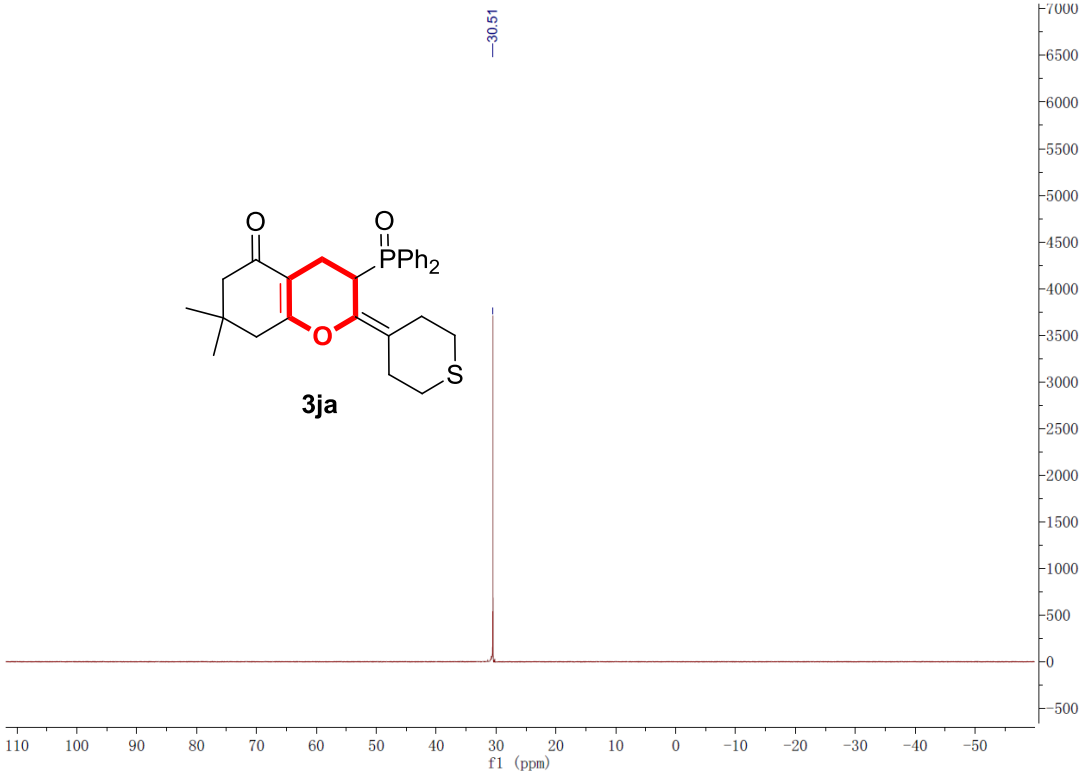

30.65
O
O
PPh2
O
O
3ia
f1 (ppm)

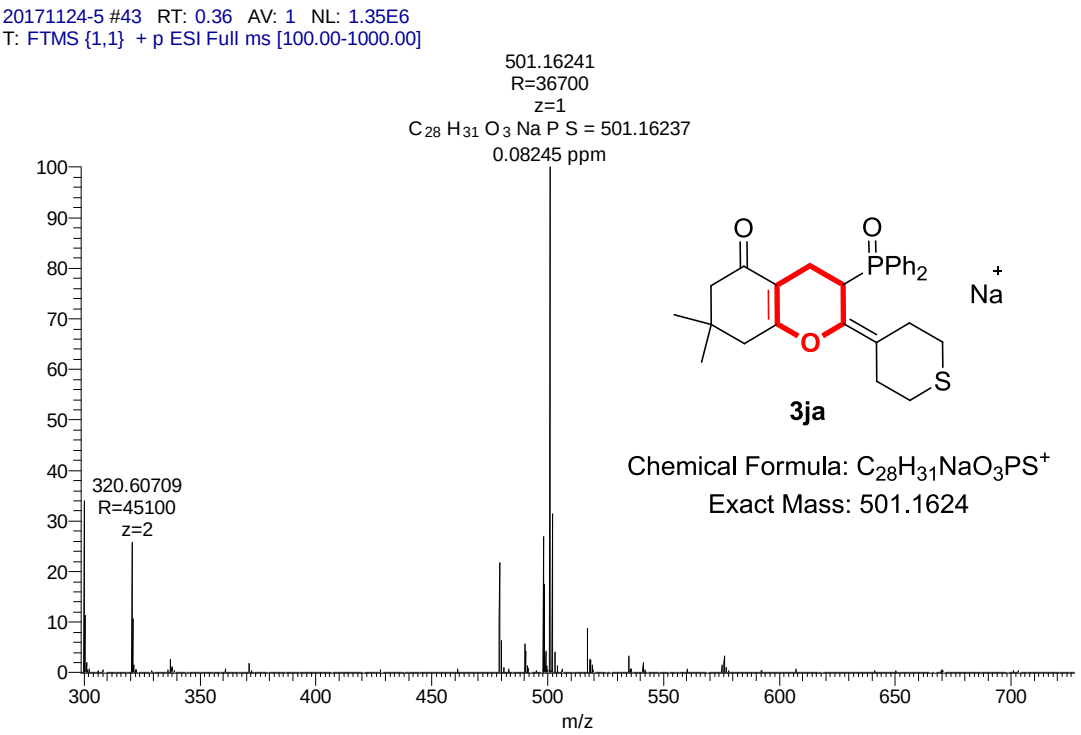
20171124-4 #30-31 RT: 0.26-0.27 AV: 2 NL: 3.50E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

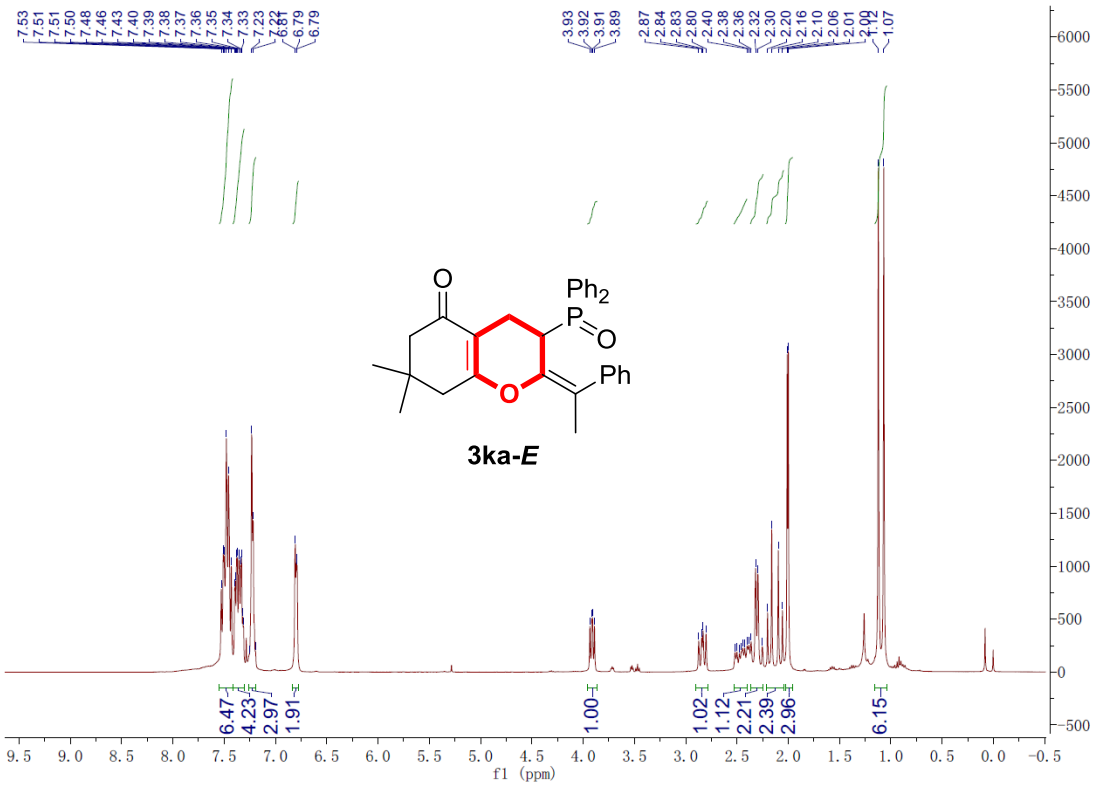


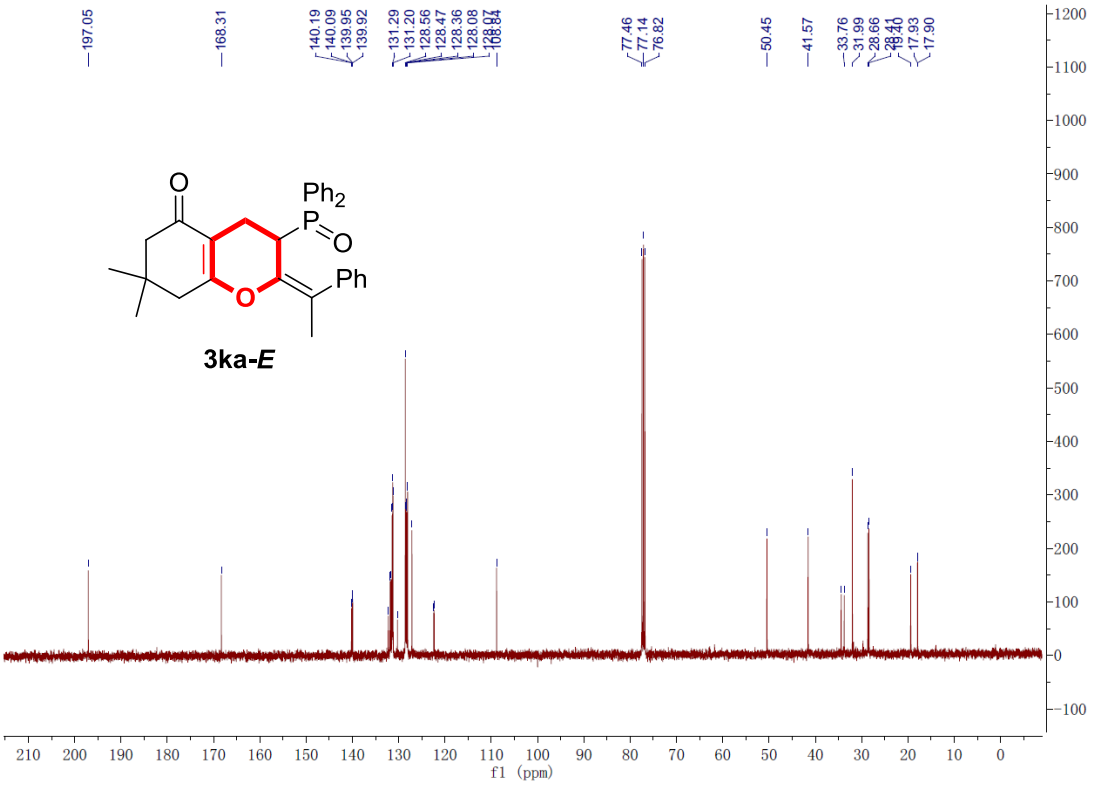



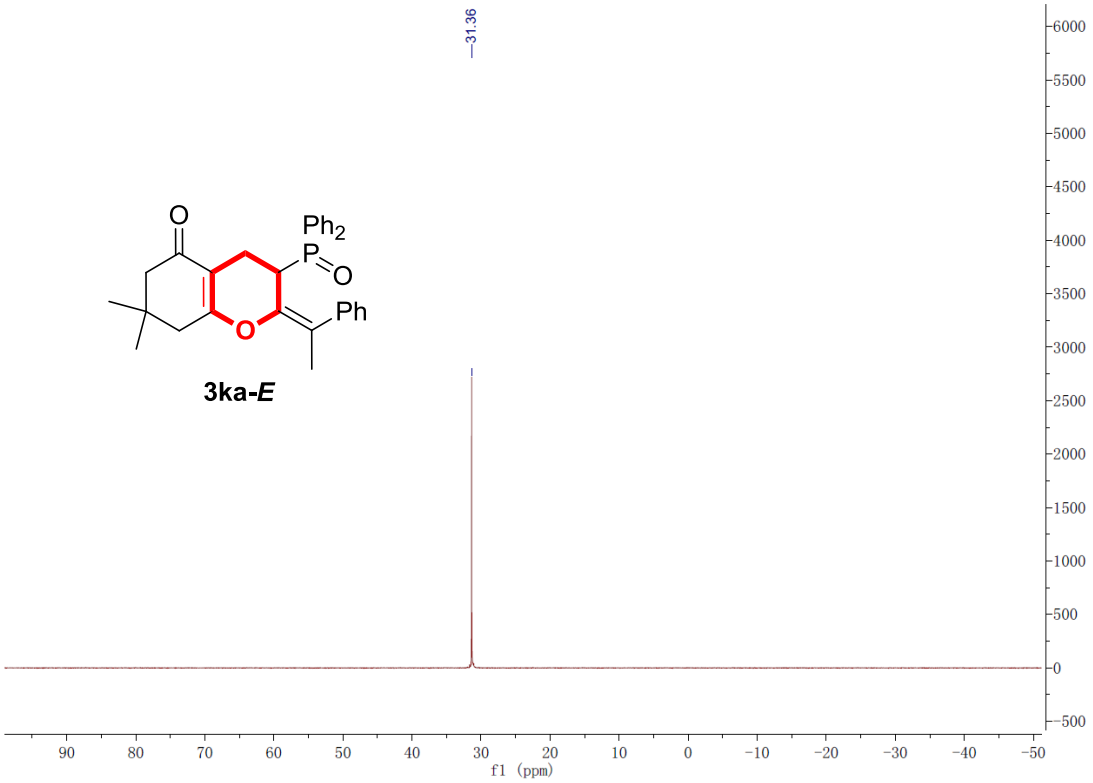

196.98
167.69
132.22
132.19
132.08
132.05
131.63
131.54
131.45
131.36
128.80
128.68
128.60
128.48
121.09
121.00
108.00
77.45
77.13
76.81
50.37
41.36
31.89
28.96
28.72
28.63
18.80
18.64
O
O
PPh2
O
S
3ja
f1 (ppm)


30.51
O
O
PPh2
O
S
3ja
f1 (ppm)

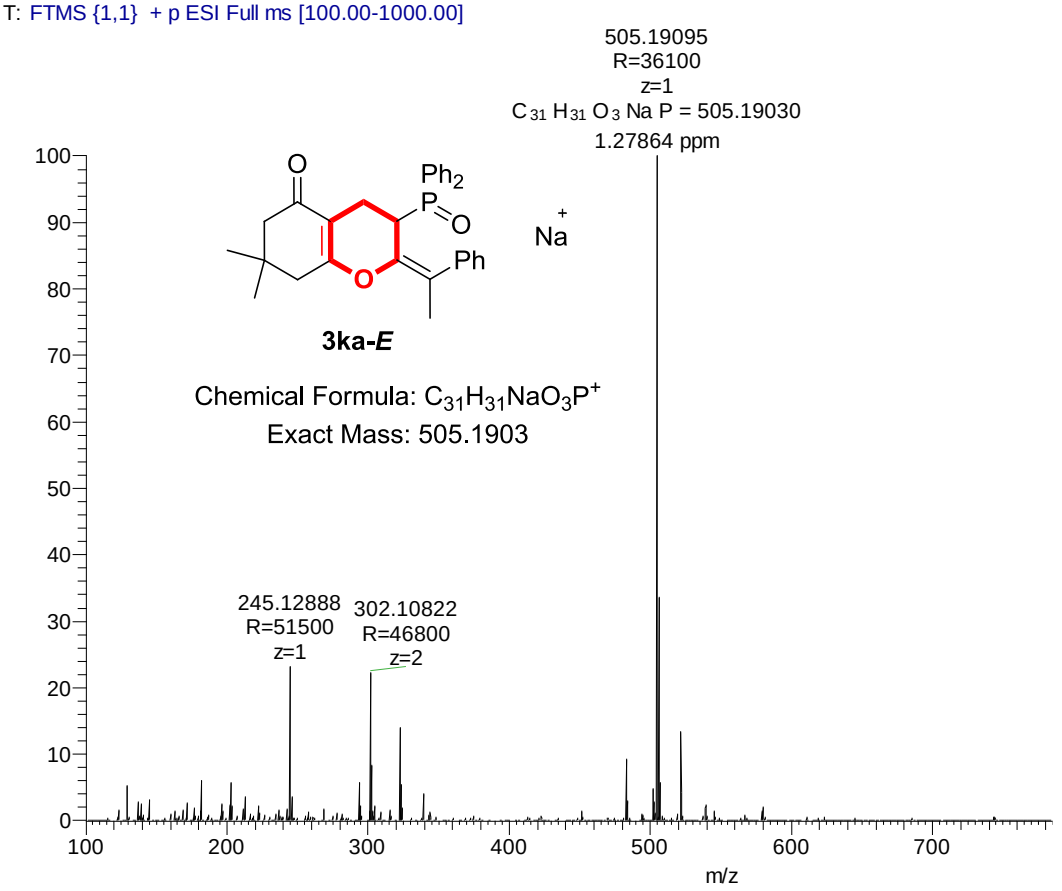

20171124-5 #43 RT: 0.36 AV: 1 NL: 1.35E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
501.16241
R=36700
z=1
C28 H31 O3 Na P S = 501.16237
0.08245 ppm
320.60709
R=45100
z=2
m/z
3ja
Chemical Formula: C28H31NaO3PS+
Exact Mass: 501.1624

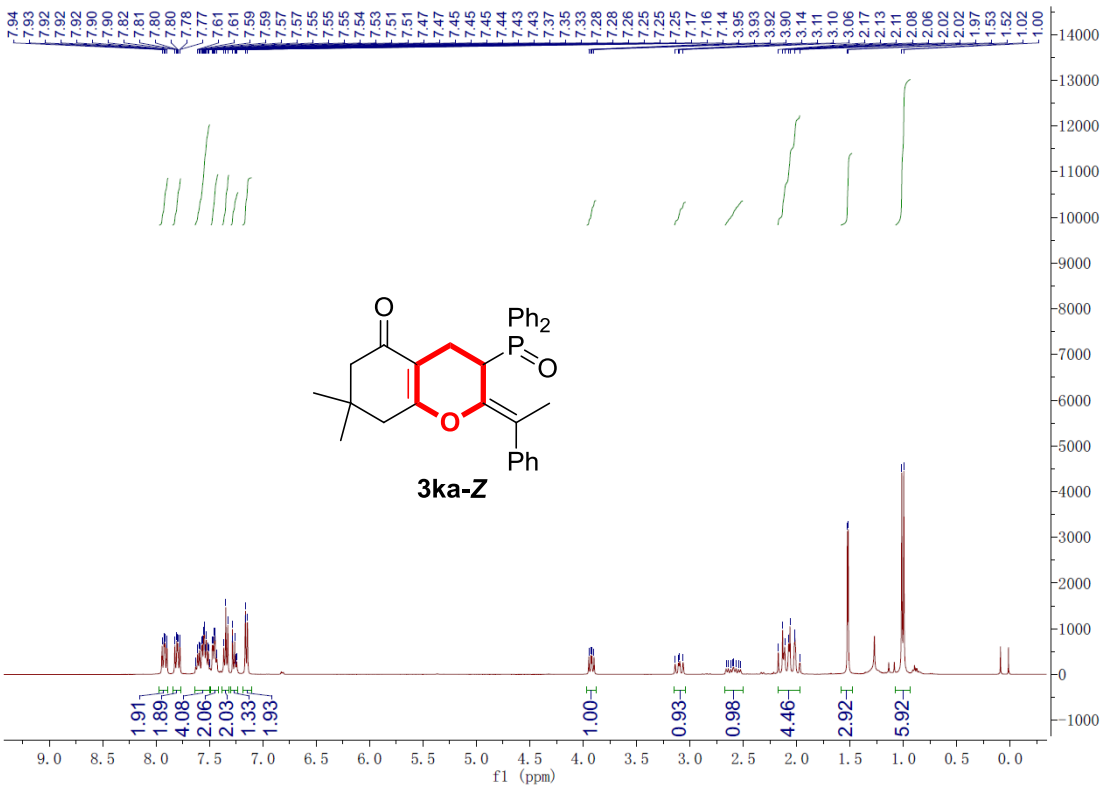

3ka-E
f1 (ppm)

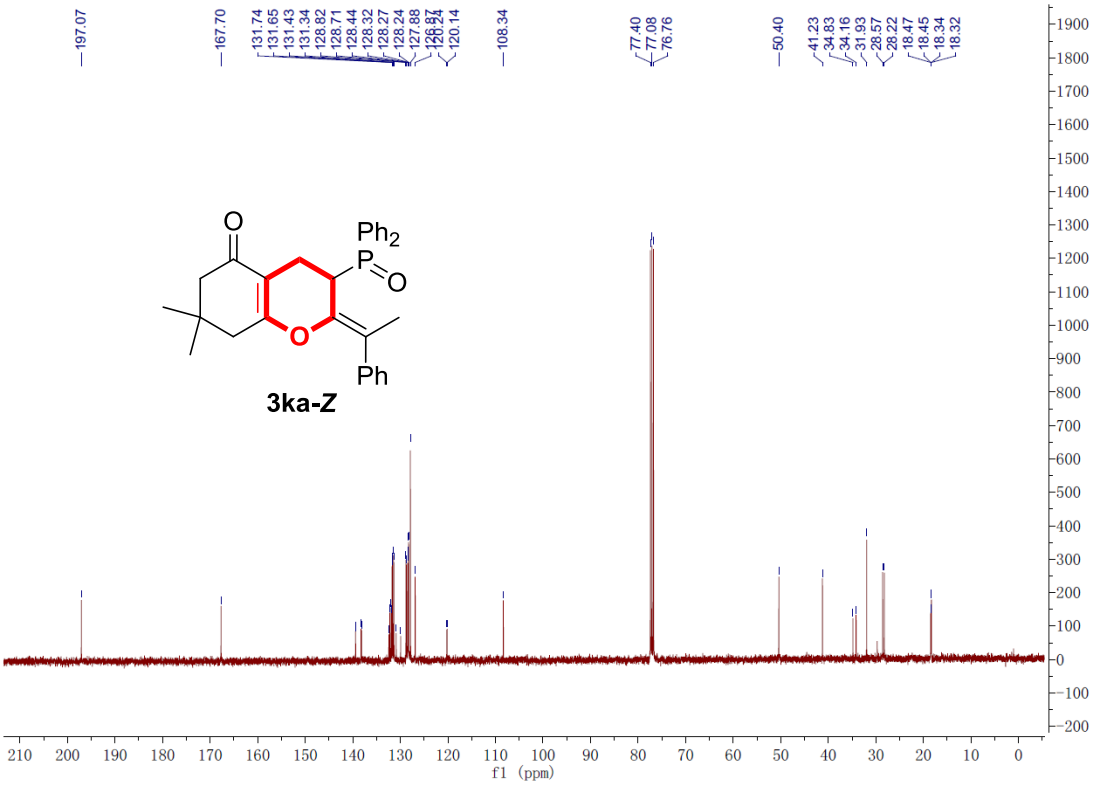

197.05
168.31
140.19
140.09
139.95
139.92
131.29
131.20
128.56
128.47
128.36
128.08
77.46
77.14
76.82
50.45
41.57
33.76
31.99
28.66
17.93
17.90
O
Ph2
P
O
Ph
O
3ka-E
f1 (ppm)

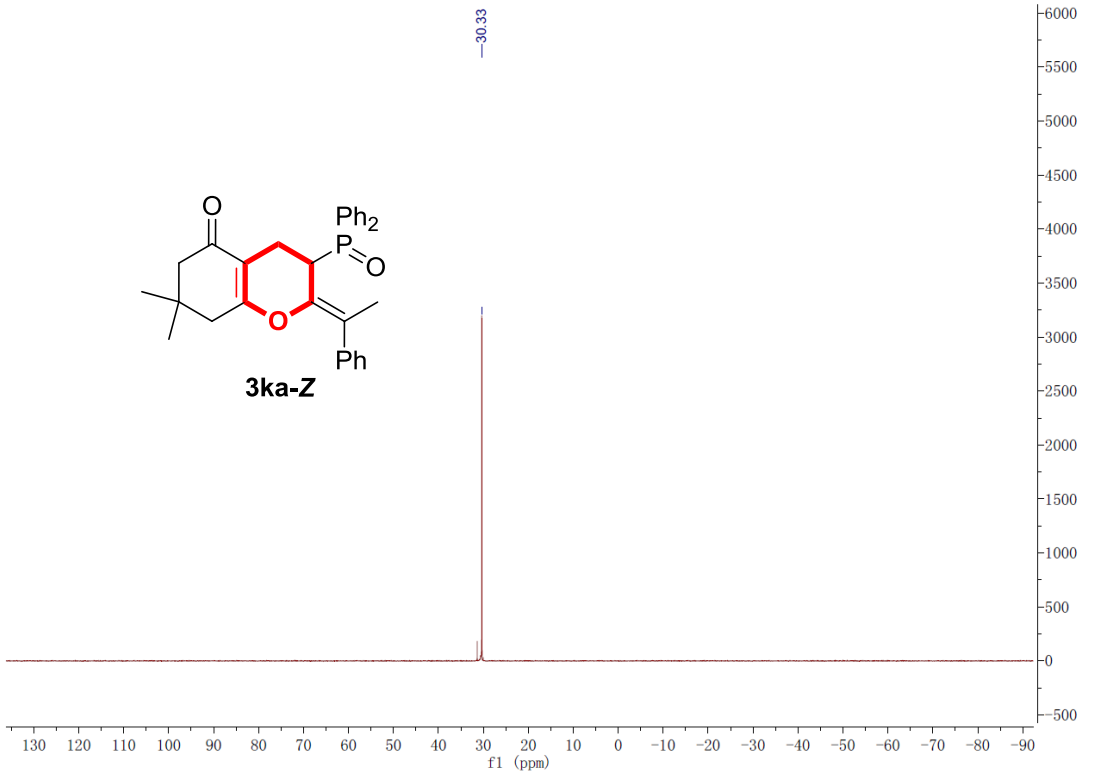

31.36
O
Ph2
P
O
Ph
O
3ka-E
f1 (ppm)

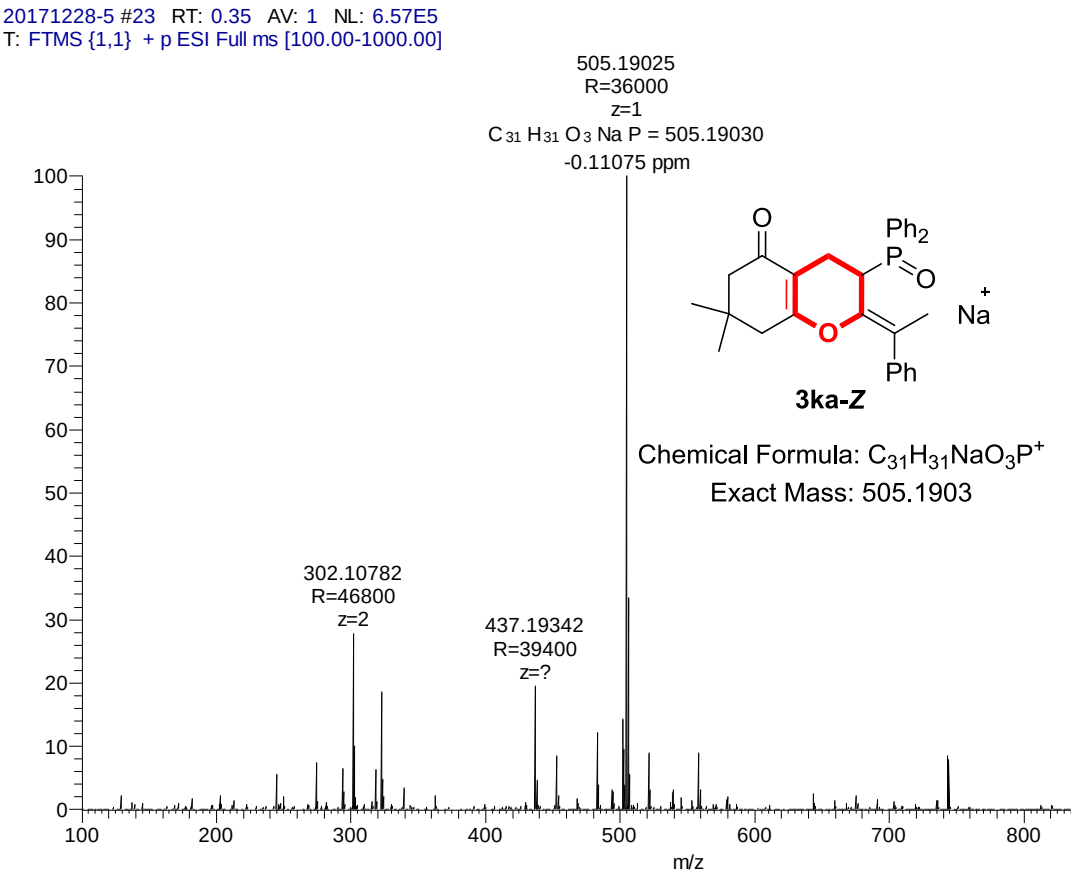
20171228-4 #27 RT: 0.41 AV: 1 NL: 2.84E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

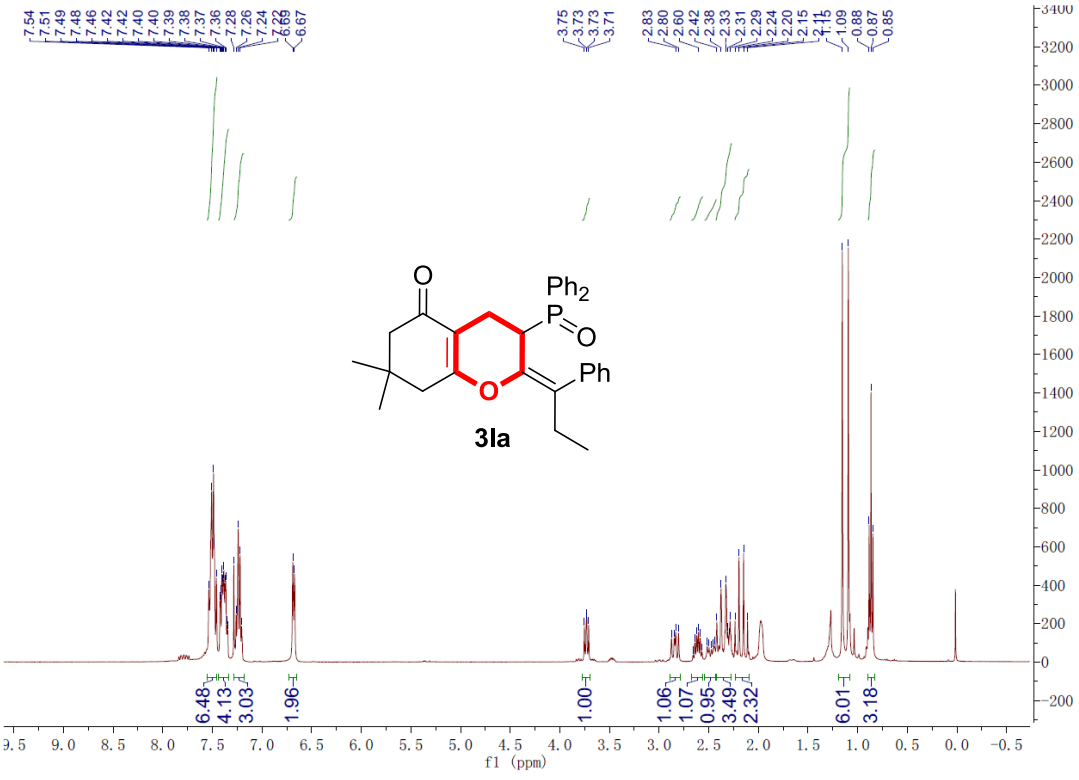


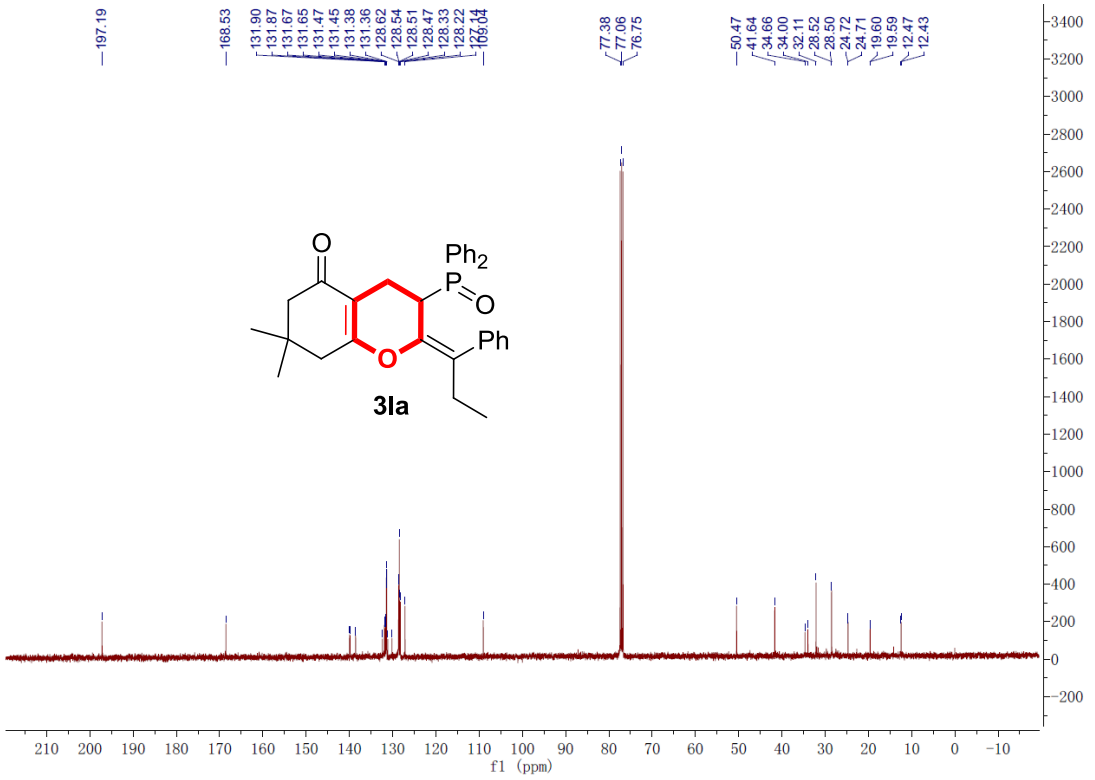



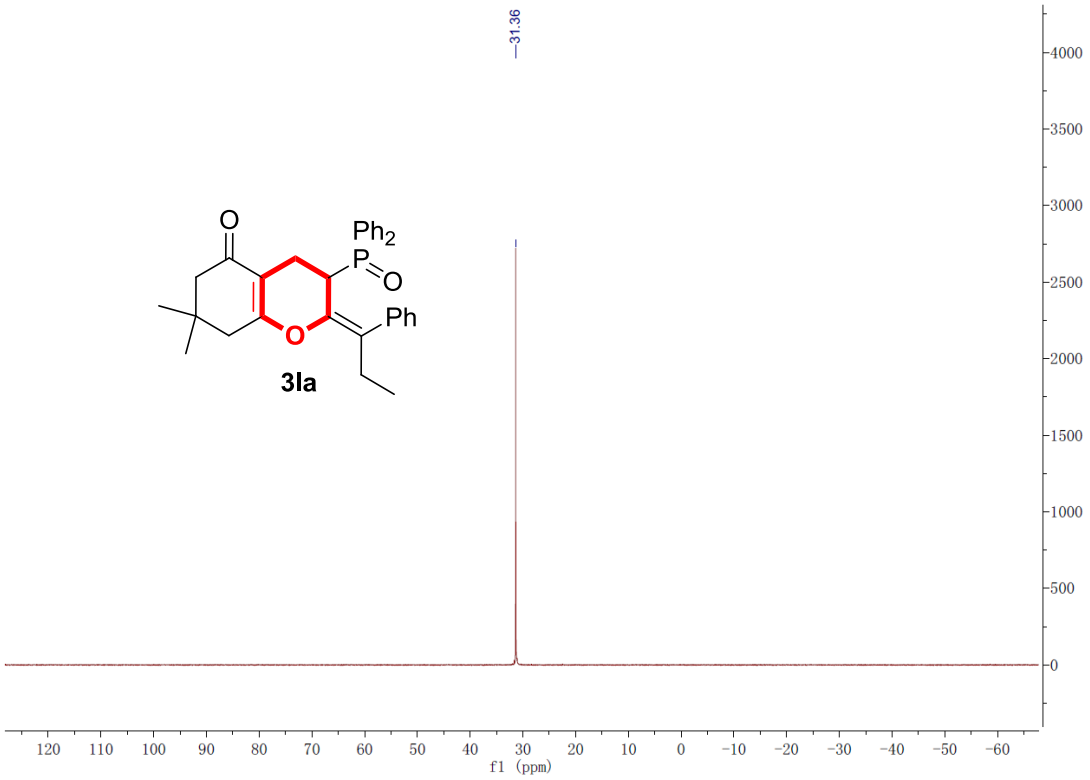

197.07
167.70
131.74
131.65
131.43
131.34
128.82
128.71
128.44
128.32
128.27
128.24
127.88
120.14
108.34
77.40
77.08
76.76
50.40
41.23
34.83
34.16
31.93
28.57
28.22
18.47
18.45
18.34
18.32
O
Ph2
P
O
O
Ph
3ka-Z
f1 (ppm)


30.33
O
Ph2
P
O
O
Ph
3ka-Z
f1 (ppm)

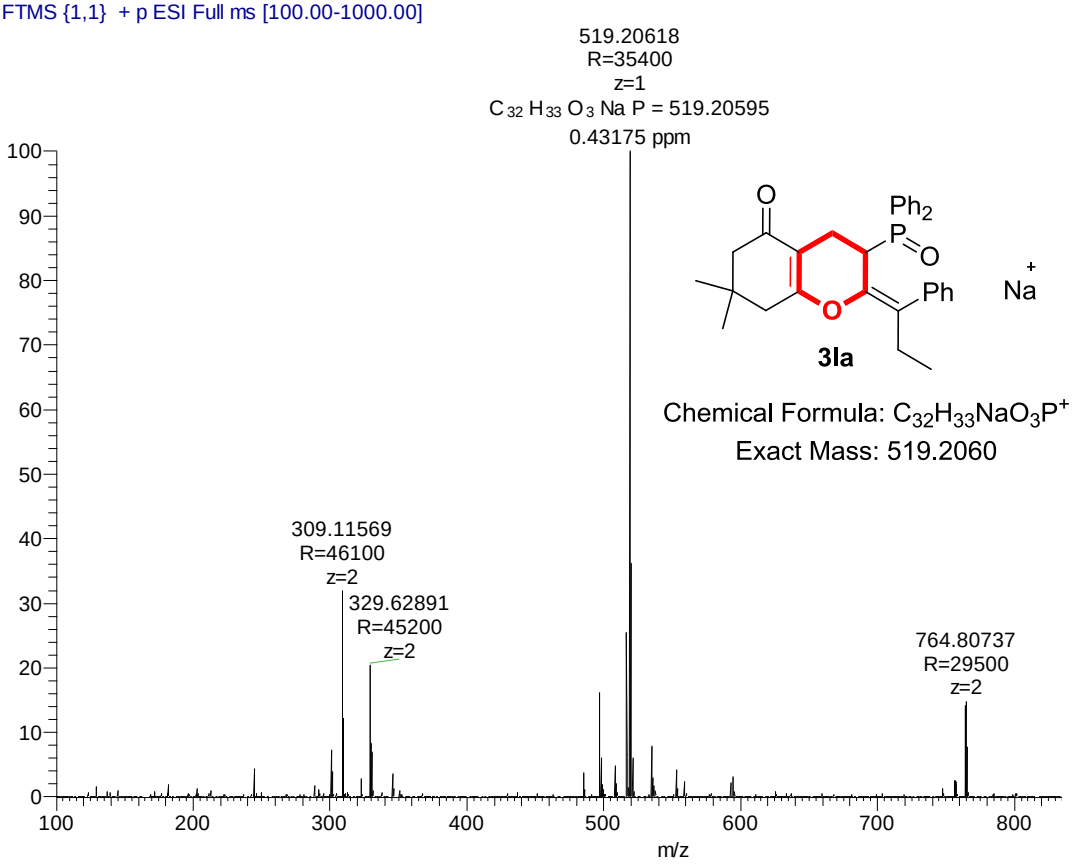

20171228-5 #23 RT: 0.35 AV: 1 NL: 6.57E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
505.19025
R=36000
z=1
C31 H31 O3 Na P = 505.19030
-0.11075 ppm
302.10782
R=46800
z=2
437.19342
R=39400
z=?
m/z
3ka-Z
Chemical Formula: C31H31NaO3P+
Exact Mass: 505.1903

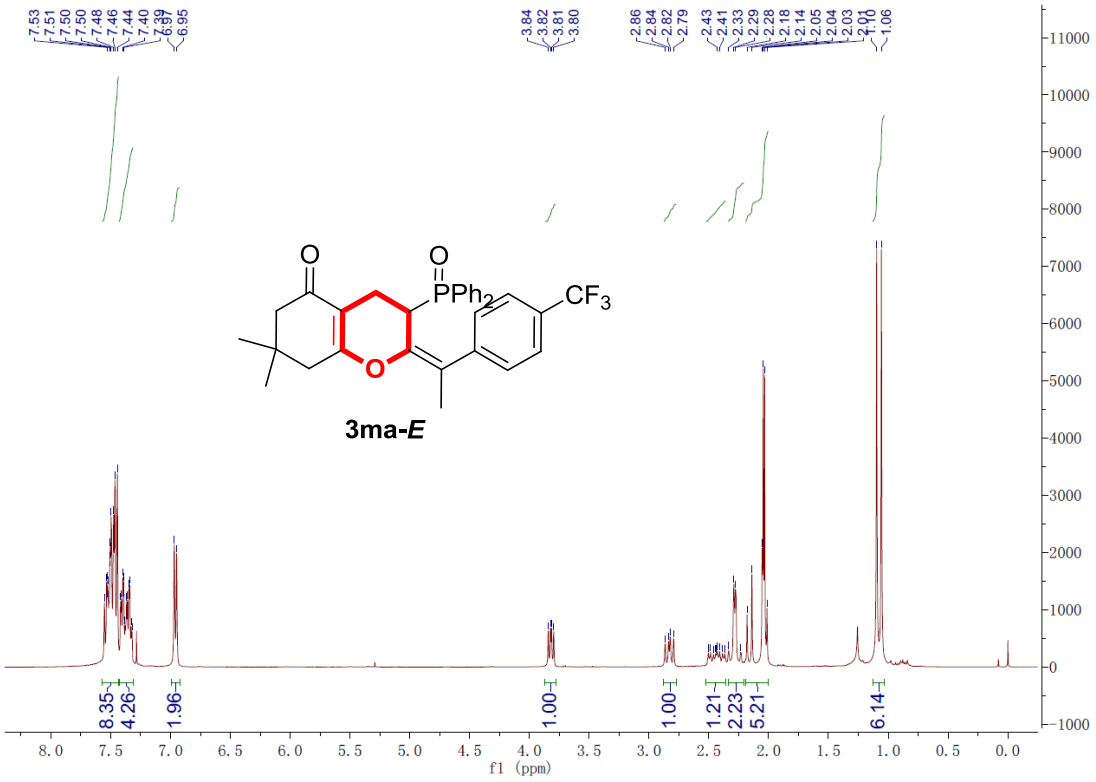

3la
f1 (ppm)

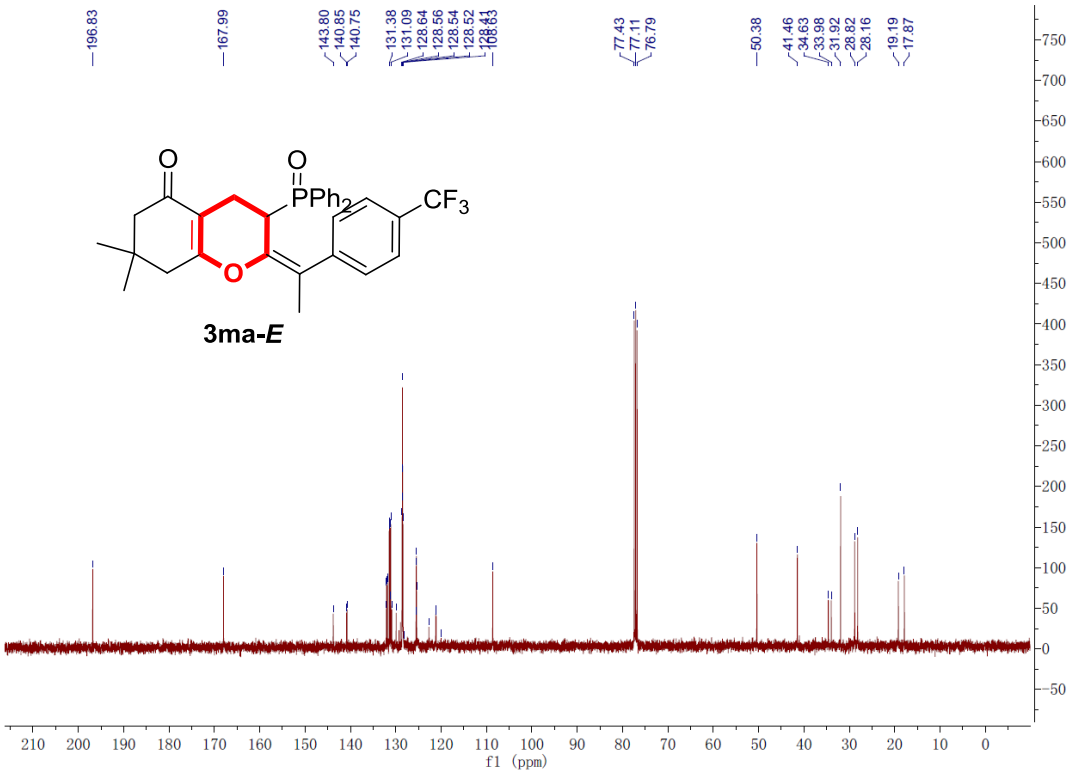

197.19
168.53
131.90
131.87
131.67
131.65
131.47
131.45
131.38
131.36
128.62
128.54
128.51
128.47
128.33
128.22
77.38
77.06
76.75
50.47
41.64
34.66
34.00
32.11
28.52
28.50
24.72
24.71
19.60
19.59
12.47
12.43
O
Ph2
P
O
Ph
O
3Ia
f1 (ppm)

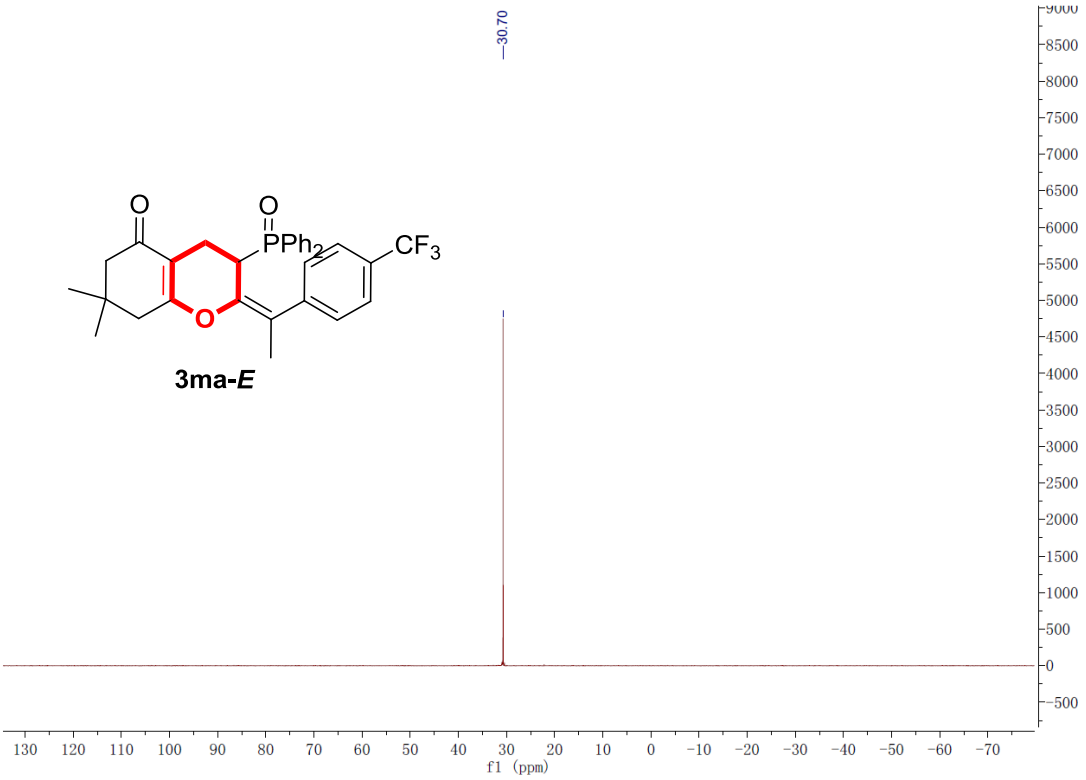

31.36
O
Ph2
P
O
Ph
O
3Ia
f1 (ppm)

20171228-3 #27 RT: 0.40 AV: 1 NL: 8.51E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

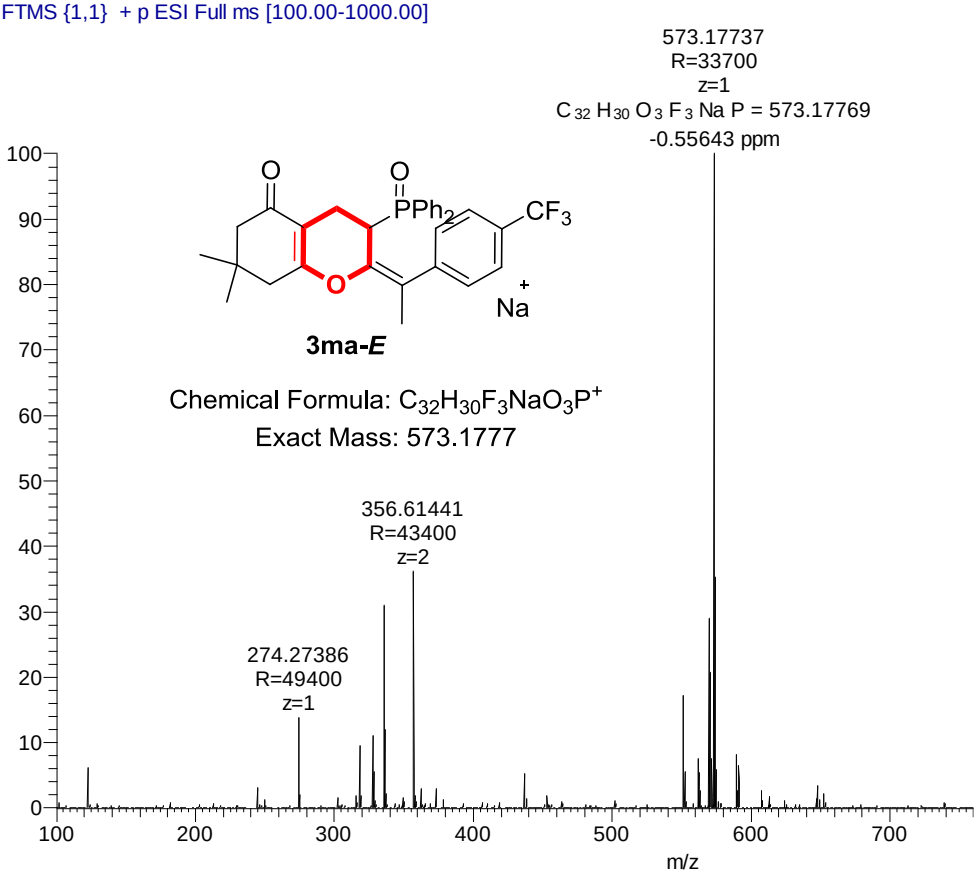


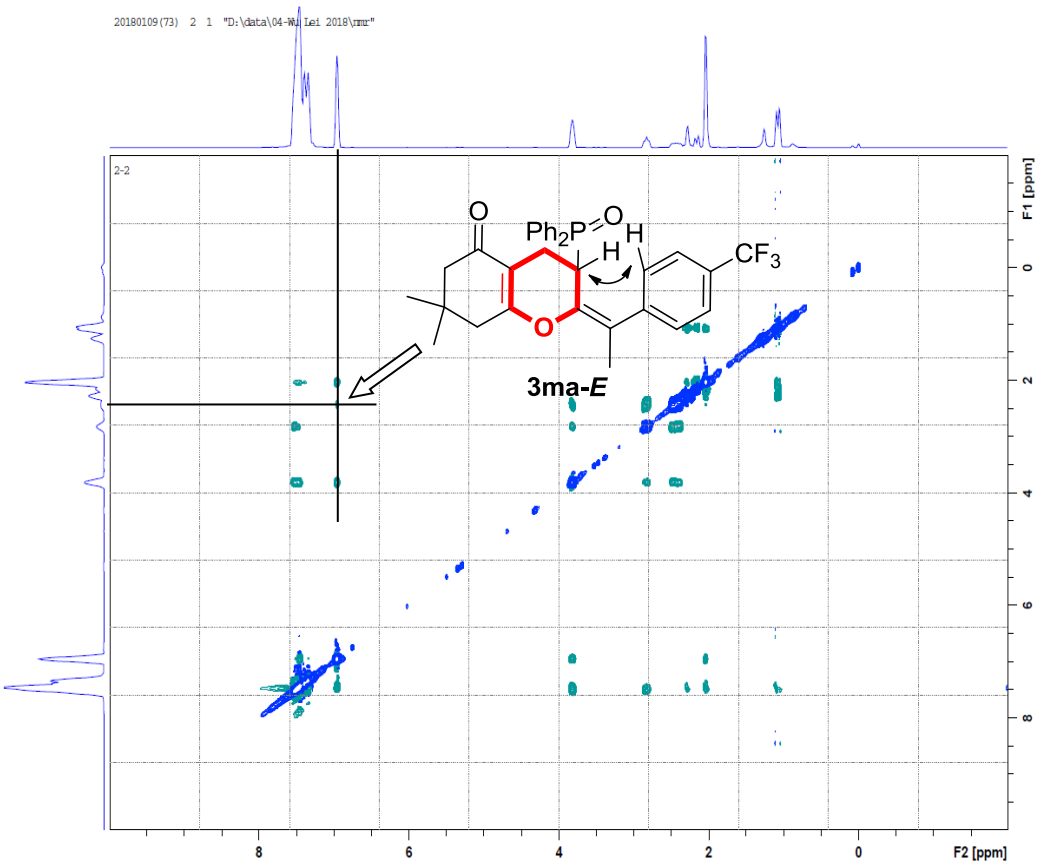



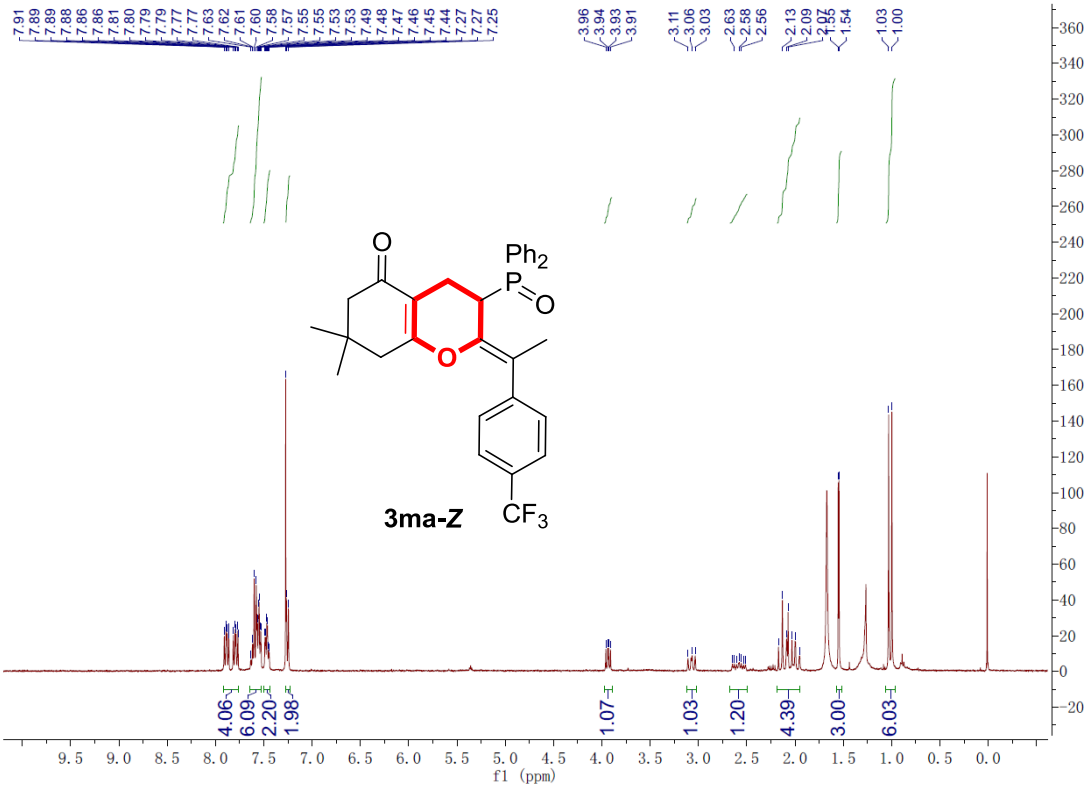

196.83
167.99
143.80
140.85
140.75
131.38
131.09
128.64
128.56
128.54
128.52
77.43
77.11
76.79
50.38
41.46
34.63
33.98
31.92
28.82
28.16
19.19
17.87
O
O
PPh2
CF3
O
3ma-E
f1 (ppm)

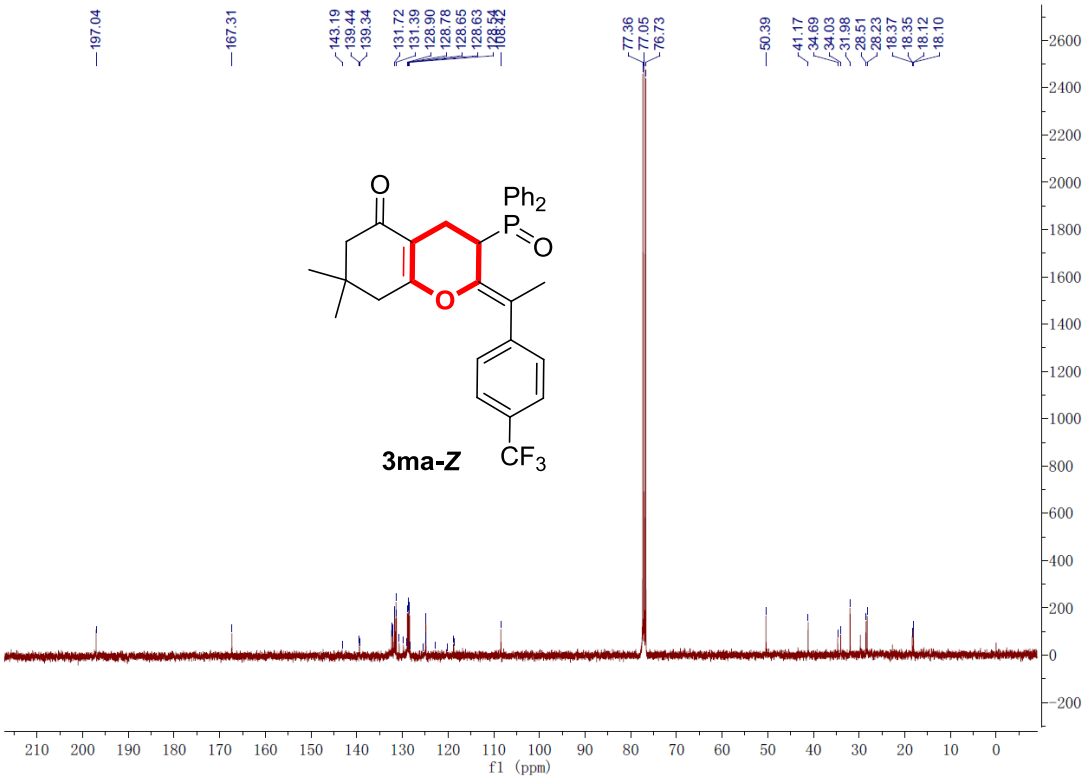

30.70
O
O
PPh2
CF3
O
3ma-E
f1 (ppm)

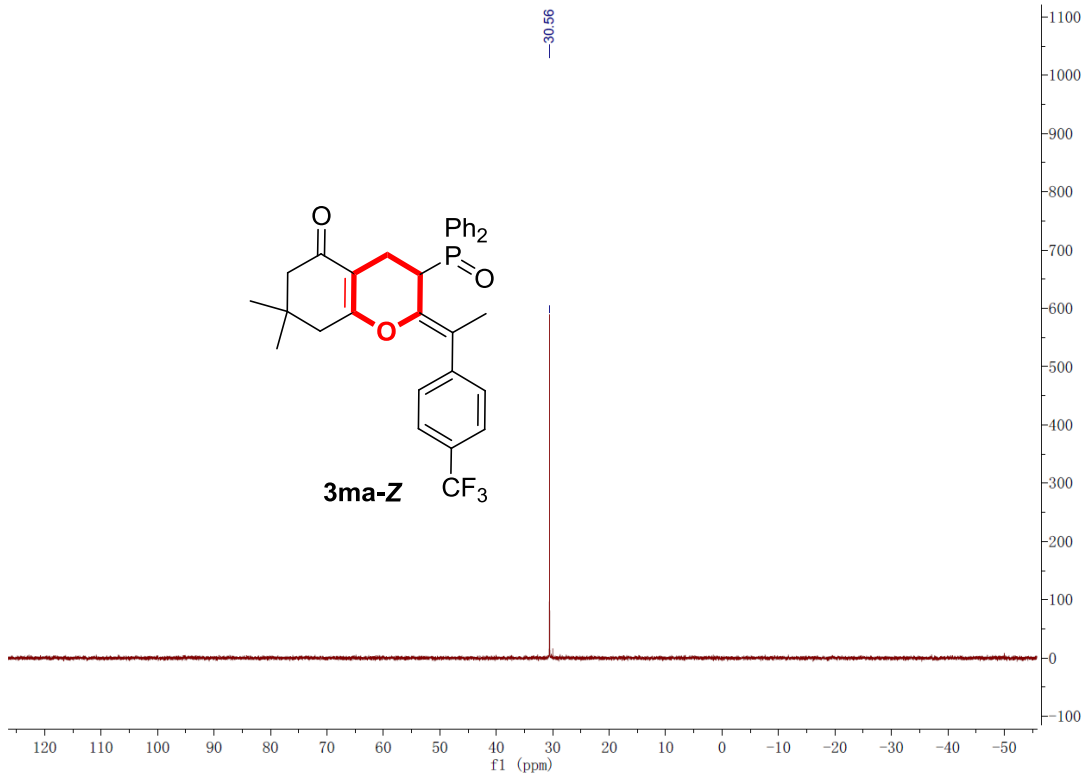
20171228-6 #15 RT: 0.24 AV: 1 NL: 1.31E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



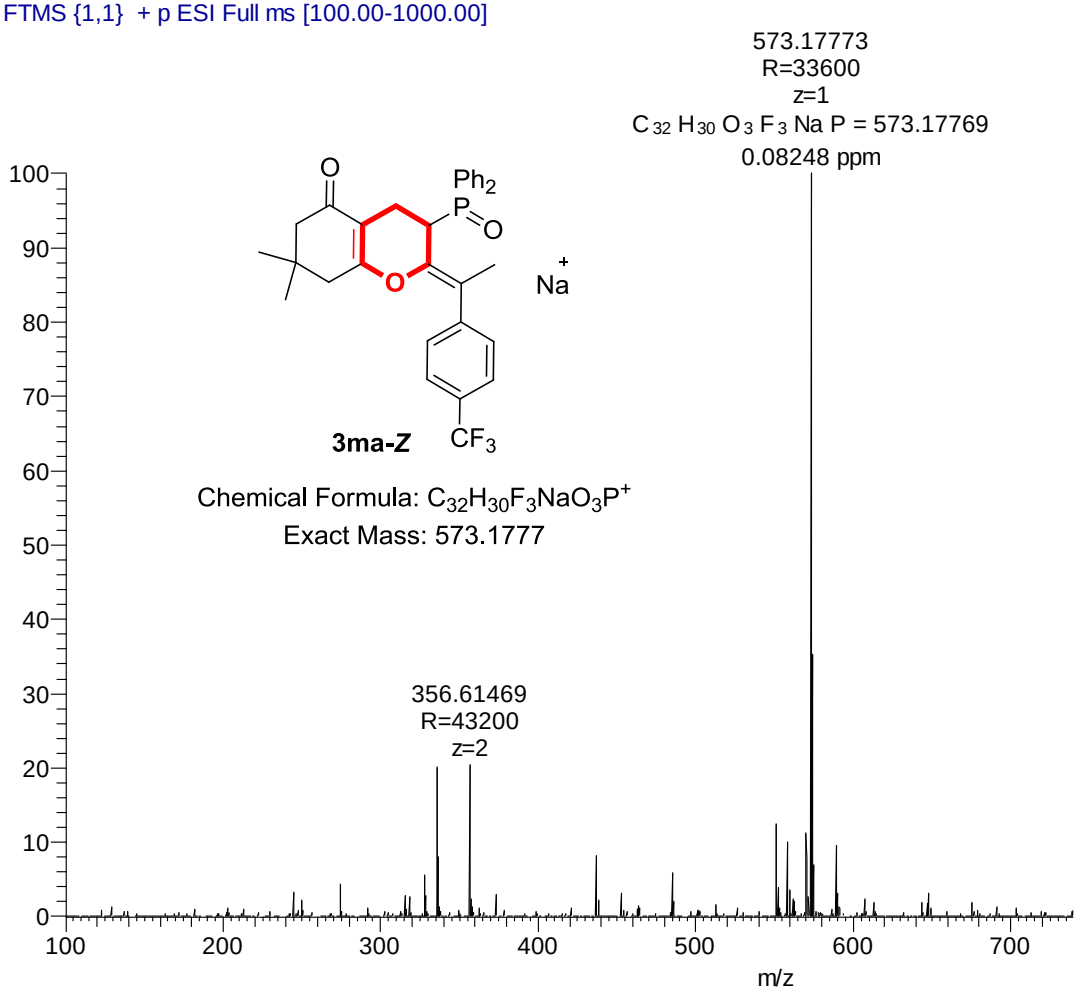



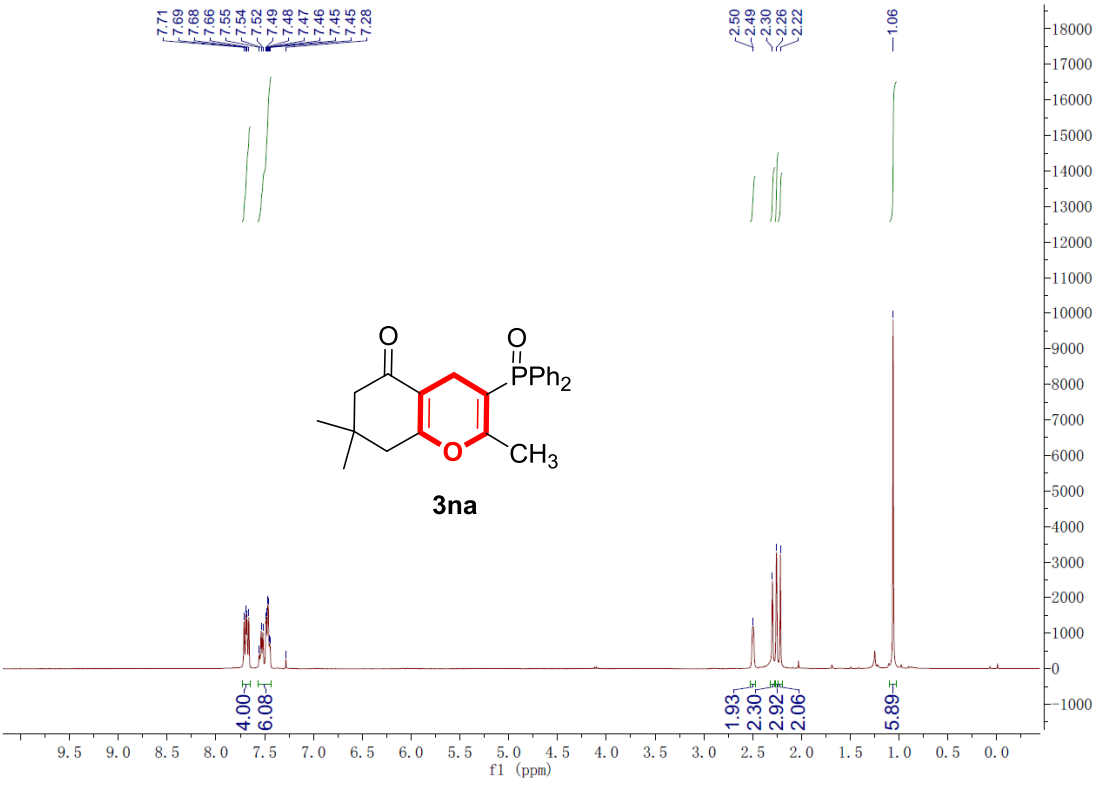

3ma-Z
f1 (ppm)

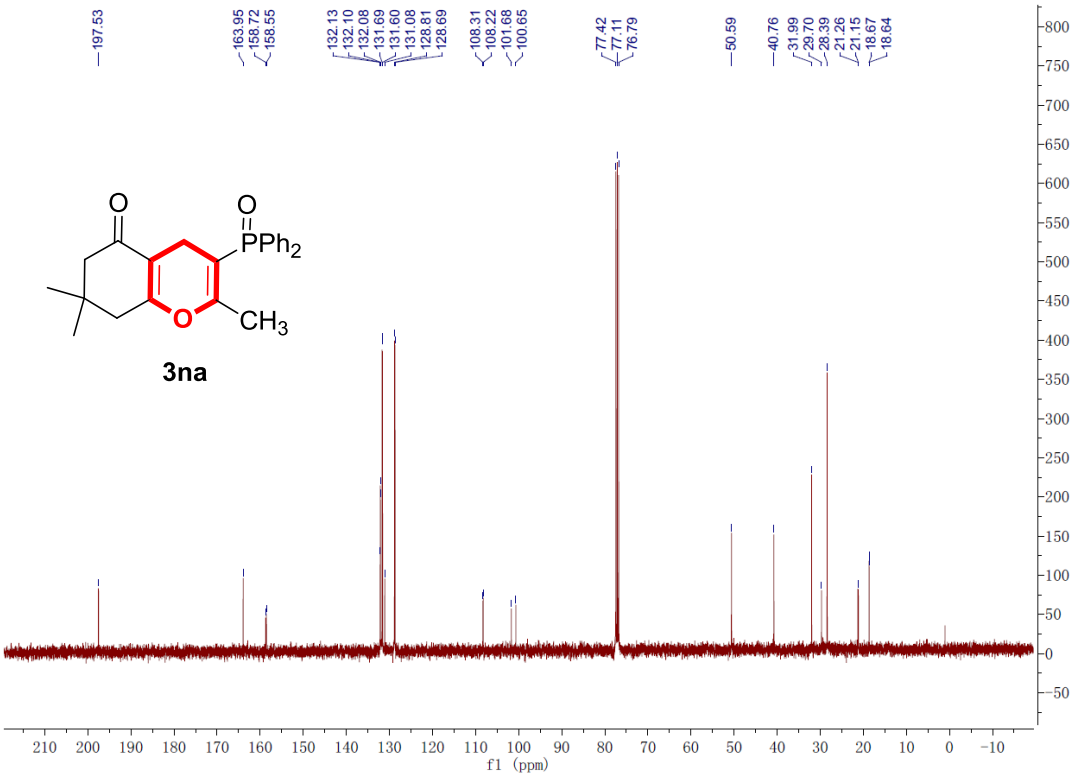

3ma-Z
f1 (ppm)

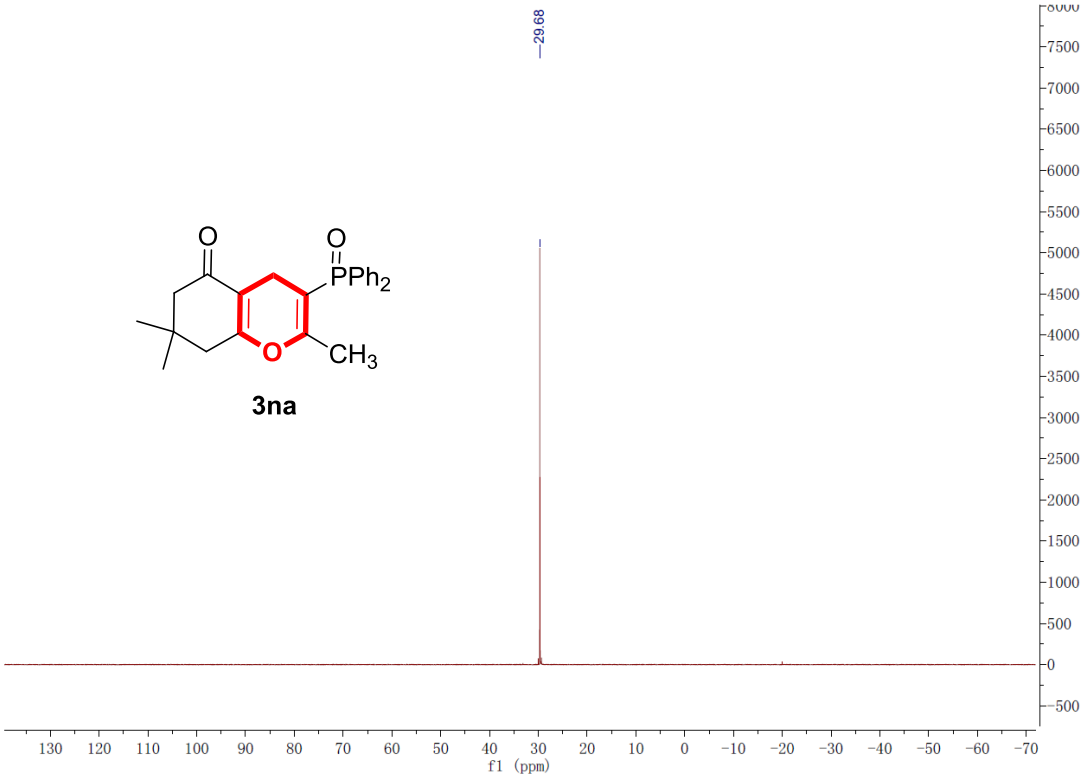


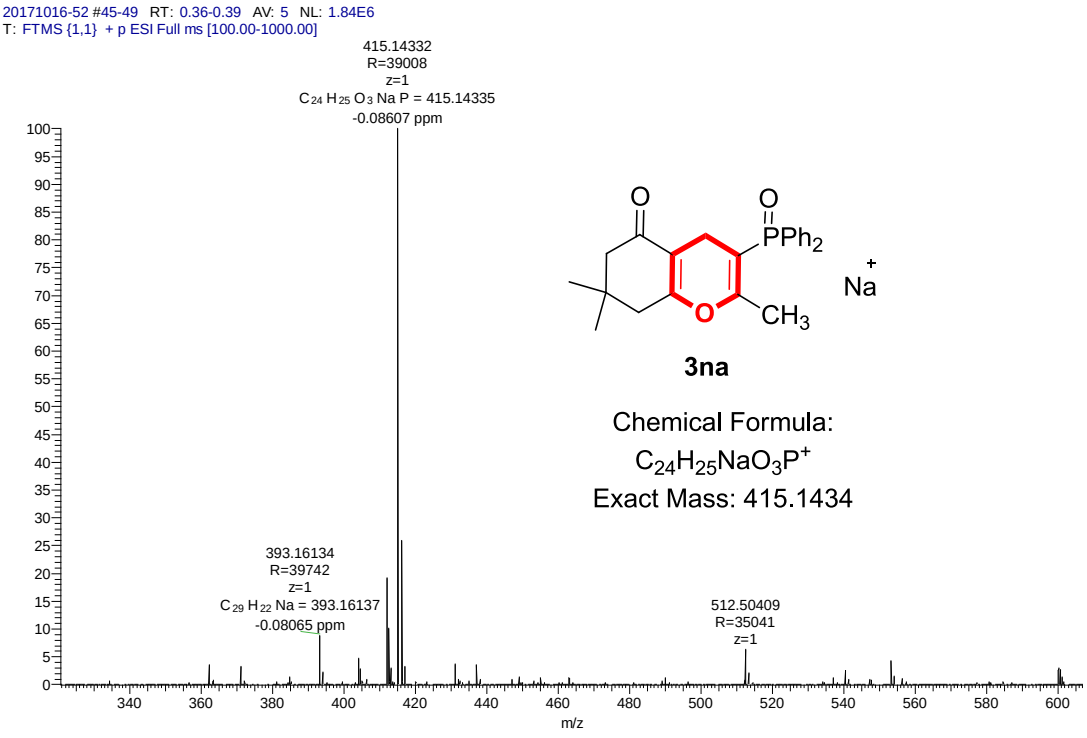

20171228-7 #25 RT: 0.38 AV: 1 NL: 8.18E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]




7.71
7.69
7.68
7.66
7.55
7.54
7.52
7.49
7.48
7.47
7.46
7.45
7.45
7.28
2.50
2.49
2.30
2.26
2.22
1.06
O
O
PPh2
O
CH3
3na
4.00
6.08
1.93
2.30
2.92
2.06
5.89
f1 (ppm)


197.53
163.95
158.72
158.55
132.13
132.10
132.08
131.69
131.60
131.08
128.81
128.69
108.31
108.22
101.68
100.65
77.42
77.11
76.79
50.59
40.76
31.99
29.70
28.39
21.26
21.15
18.67
18.64
O
O
PPh2
O
CH3
3na
f1 (ppm)



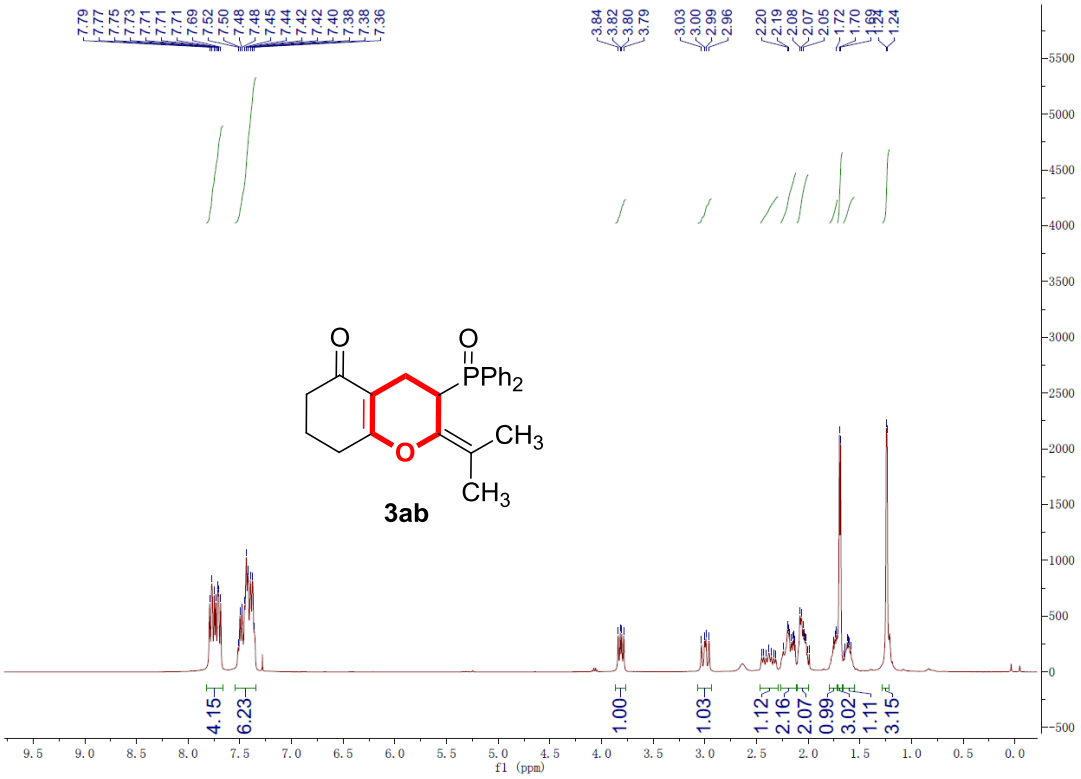



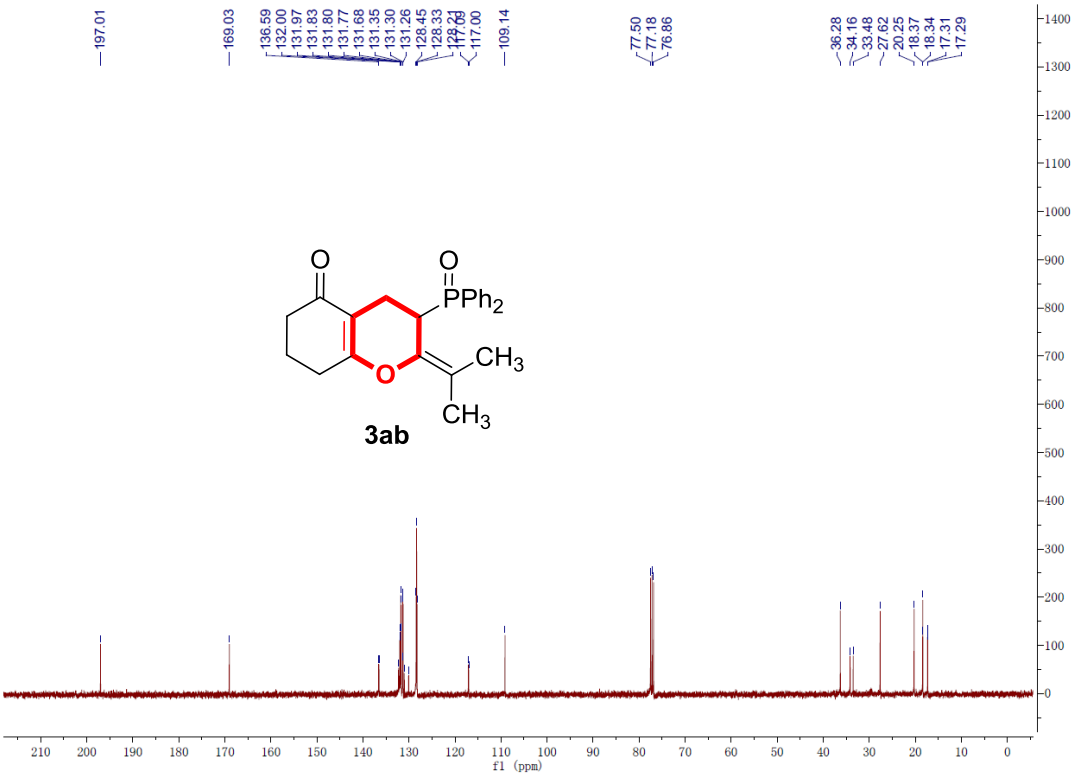


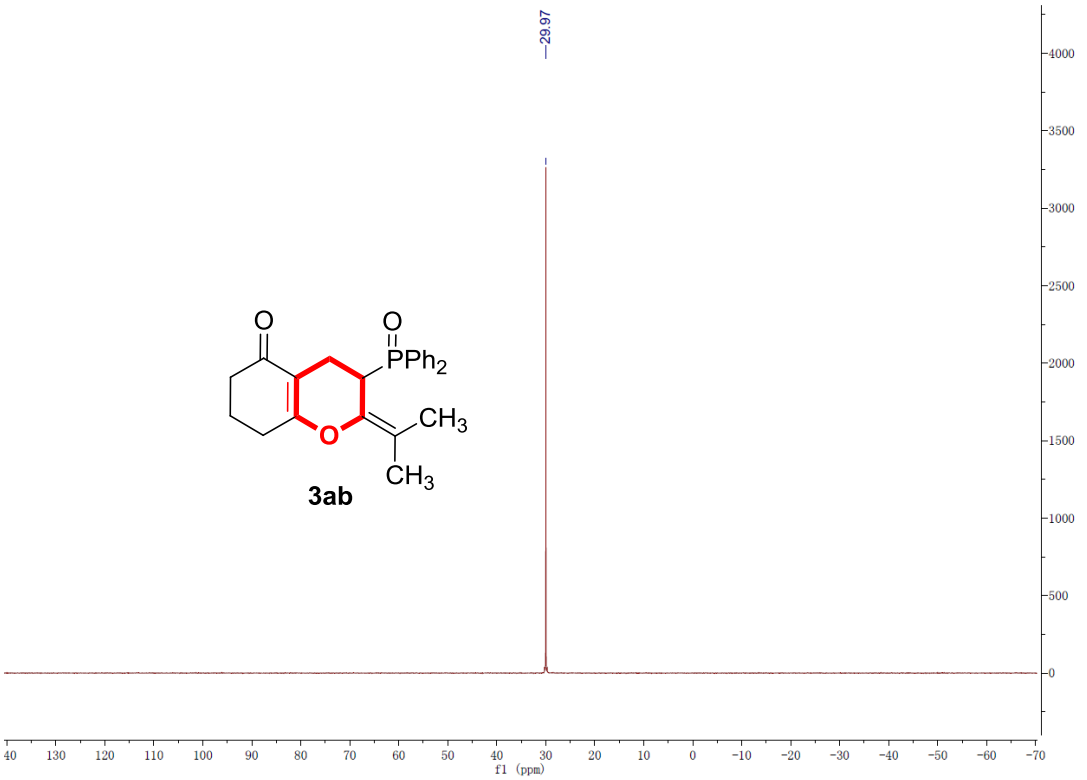


**3na**

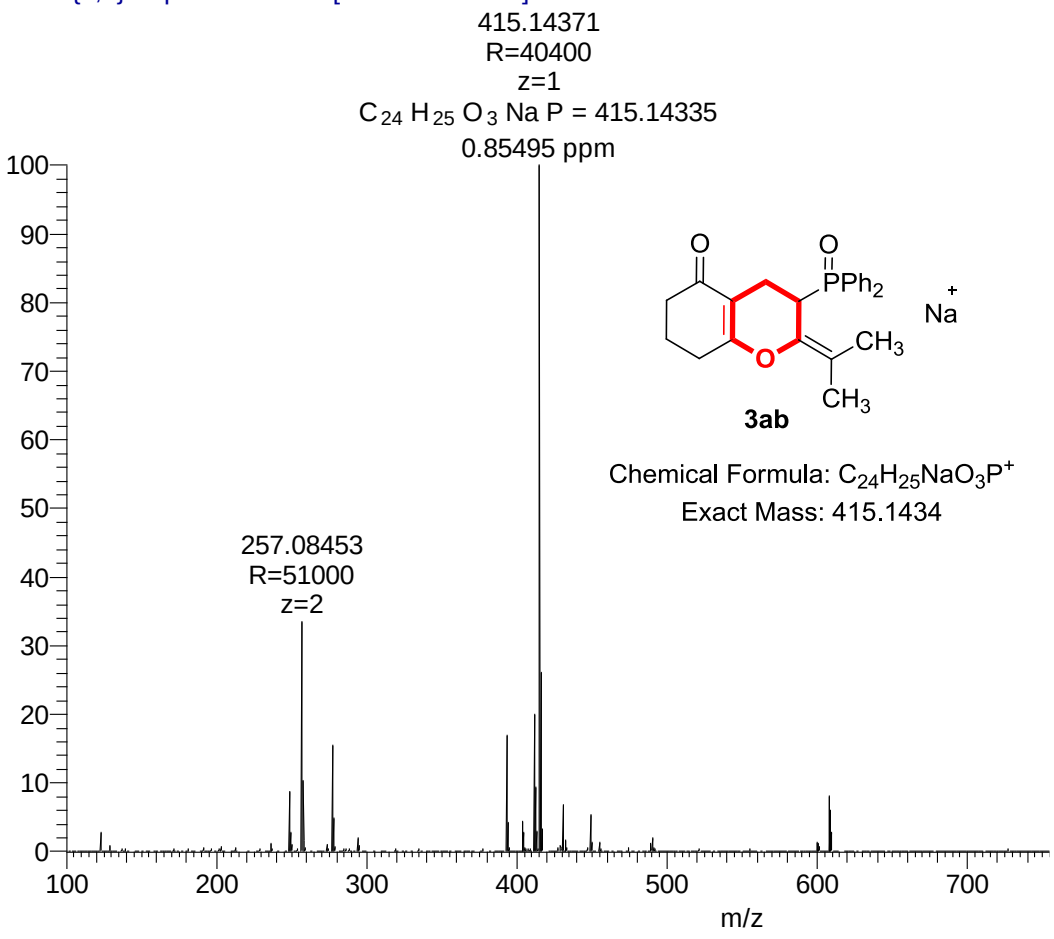
Chemical Formula:
$C_{24}H_{25}NaO_3P^+$
Exact Mass: 415.1434

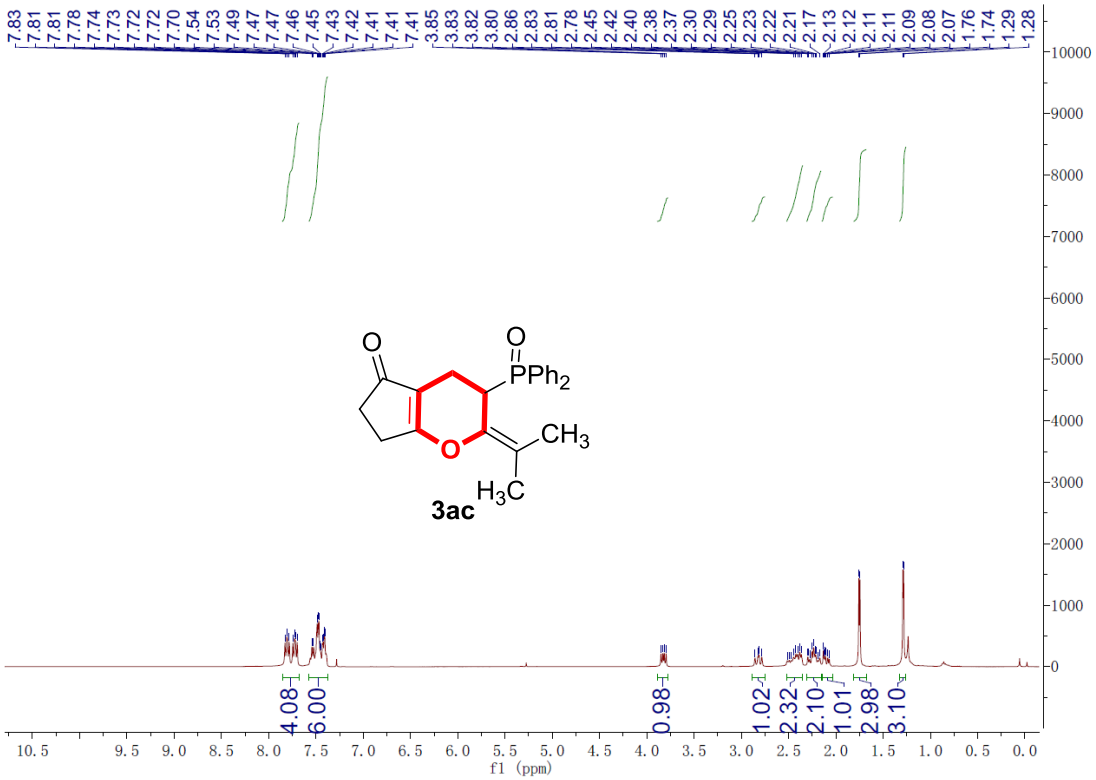

7.79
7.77
7.75
7.73
7.71
7.71
7.71
7.69
7.52
7.50
7.48
7.48
7.45
7.44
7.42
7.42
7.40
7.38
7.38
7.36
3.84
3.82
3.80
3.79
3.03
3.00
2.99
2.96
2.20
2.19
2.08
2.07
2.05
1.72
1.70
1.69
1.24
O
O
PPh2
CH3
CH3
3ab
4.15
6.23
1.00
1.03
1.12
2.16
2.07
0.99
3.02
1.11
3.15
f1 (ppm)

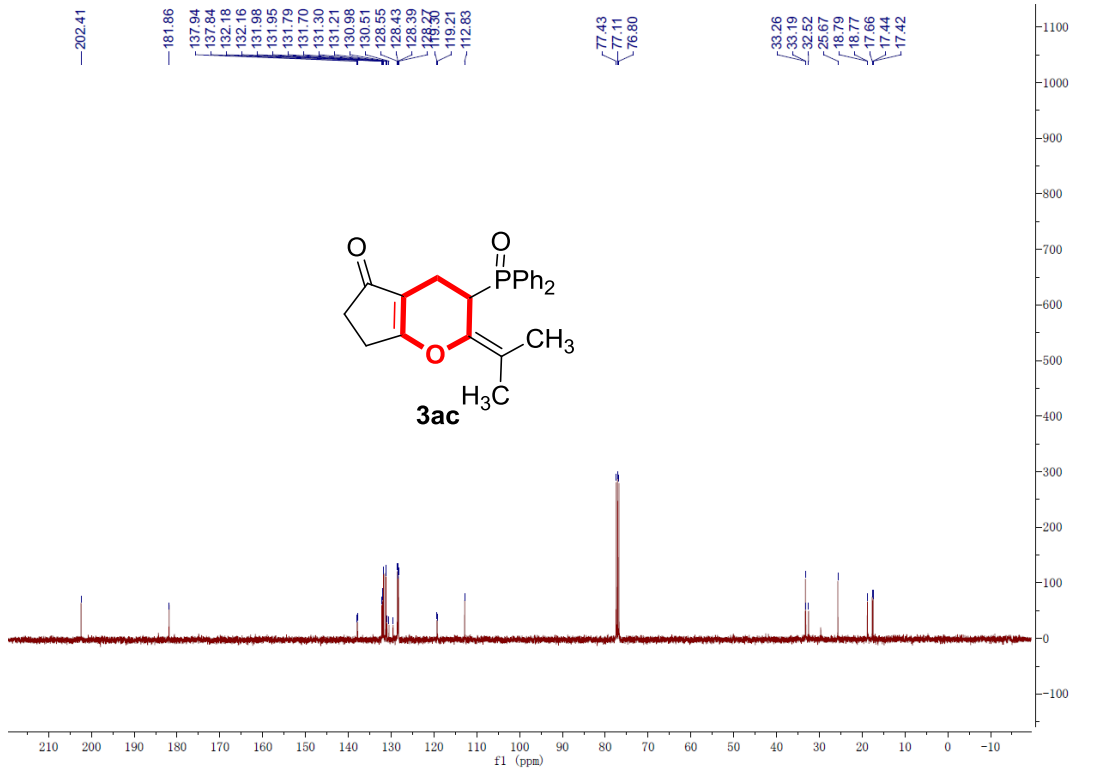

197.01
169.03
136.59
132.00
131.97
131.83
131.80
131.77
131.68
131.35
131.30
131.26
128.45
128.33
128.21
117.00
109.14
77.50
77.18
76.86
36.28
34.16
33.48
27.62
20.25
18.37
18.34
17.31
17.29
O
O
PPh2
CH3
CH3
3ab
f1 (ppm)

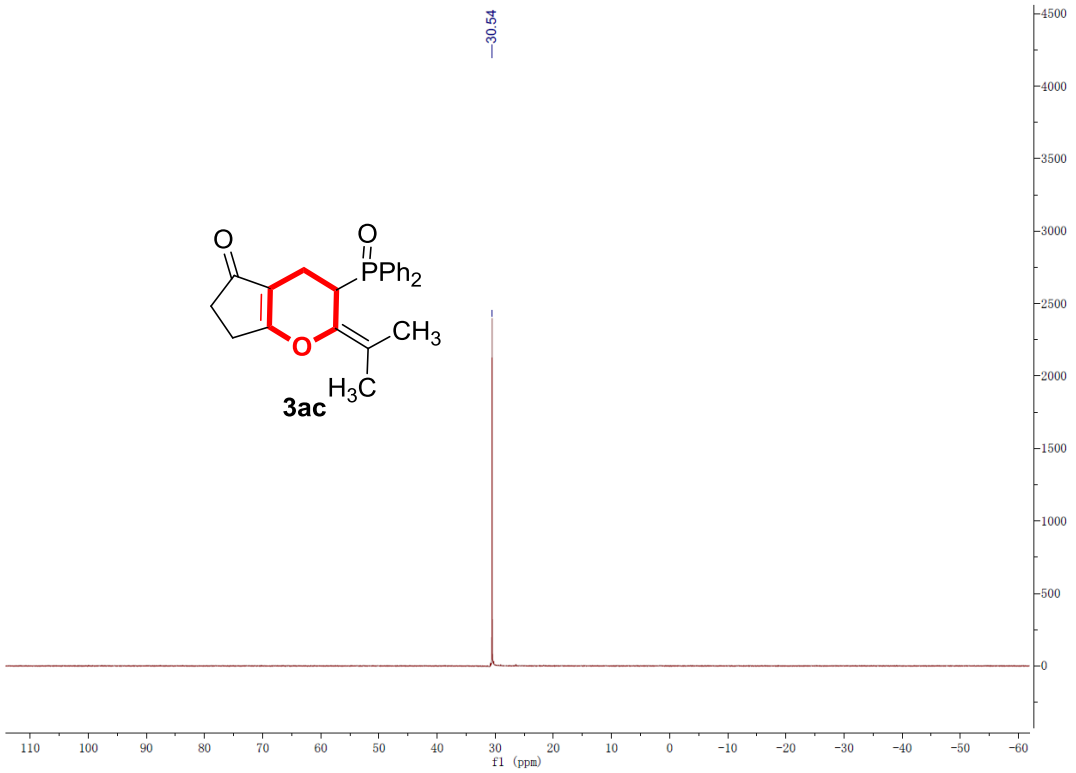



20171124-8 #37 RT: 0.33 AV: 1 NL: 1.13E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

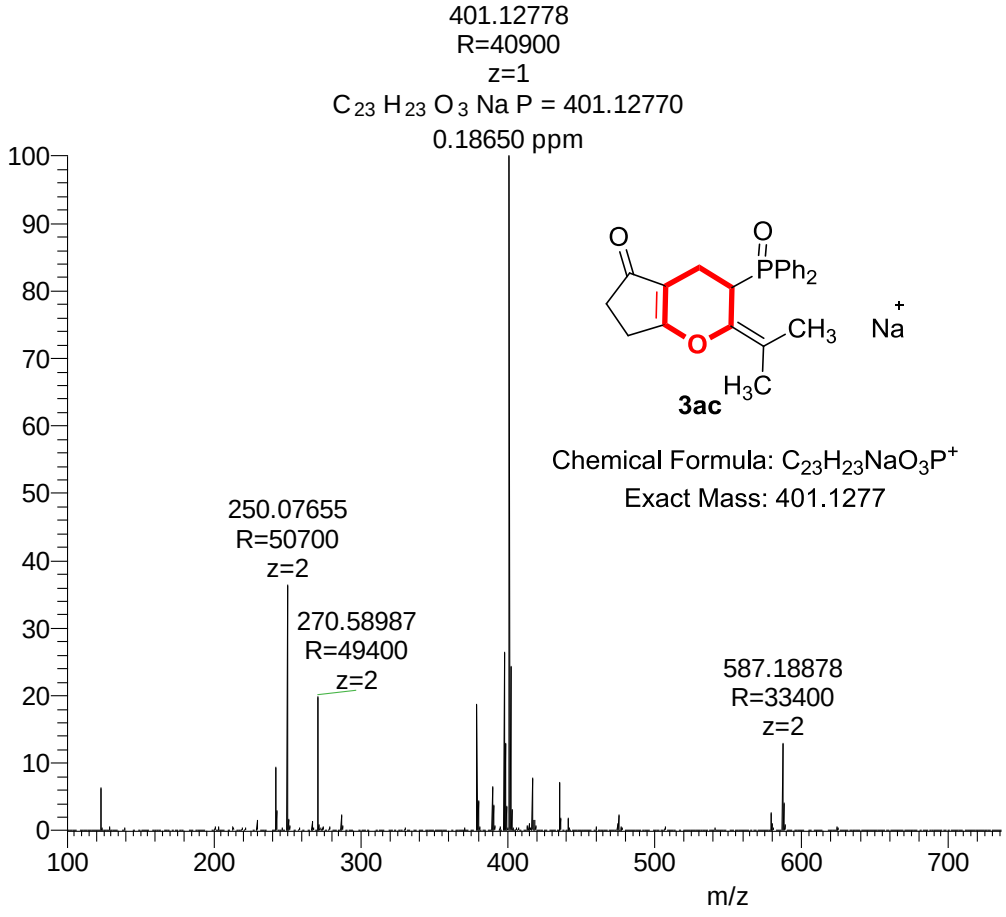


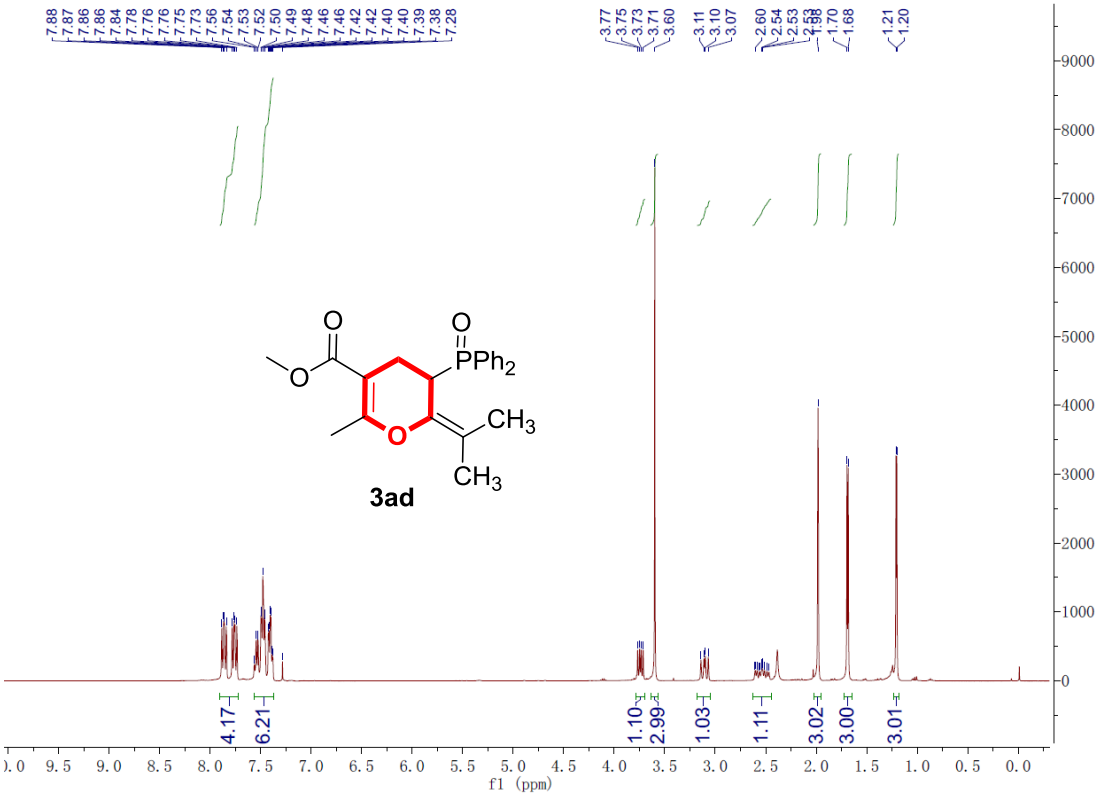

7.83 7.81 7.81 7.78 7.74 7.73 7.72 7.72 7.70 7.54 7.53 7.49 7.47 7.47 7.46 7.45 7.43 7.42 7.41 7.41 7.41 3.85 3.83 3.82 3.80 2.86 2.83 2.81 2.78 2.45 2.42 2.40 2.38 2.37 2.30 2.29 2.25 2.23 2.22 2.21 2.17 2.13 2.12 2.11 2.11 2.09 2.08 2.07 1.76 1.74 1.29 1.28
O
O
PPh2
CH3
O
H3C
3ac
4.08 6.00 0.98 1.02 2.32 2.10 1.01 2.98 3.10
f1 (ppm)

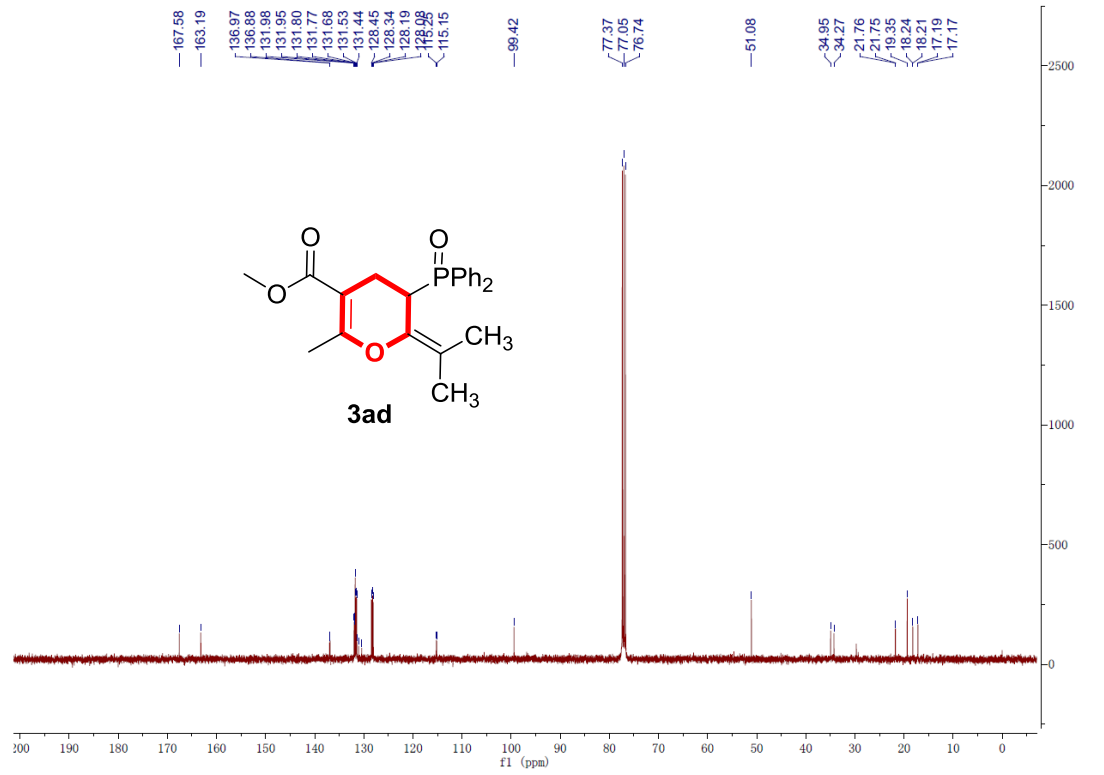

202.41
181.86
137.94 137.84 132.18 132.16 131.98 131.95 131.79 131.70 131.30 131.21 130.98 130.51 128.55 128.43 128.39 128.27 119.30 119.21 112.83
77.43 77.11 76.80
33.26 33.19 32.52 25.67 18.79 18.77 17.66 17.44 17.42
O
O
PPh2
CH3
O
H3C
3ac
f1 (ppm)

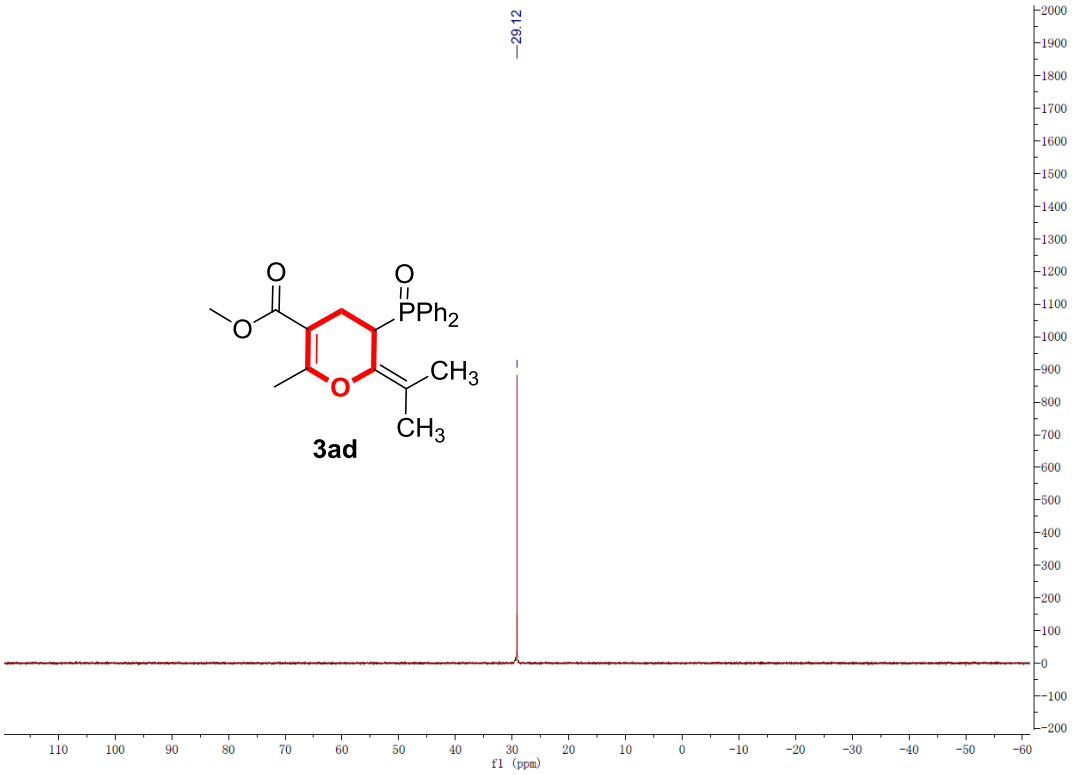



20171124-7 #31 RT: 0.29 AV: 1 NL: 1.36E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

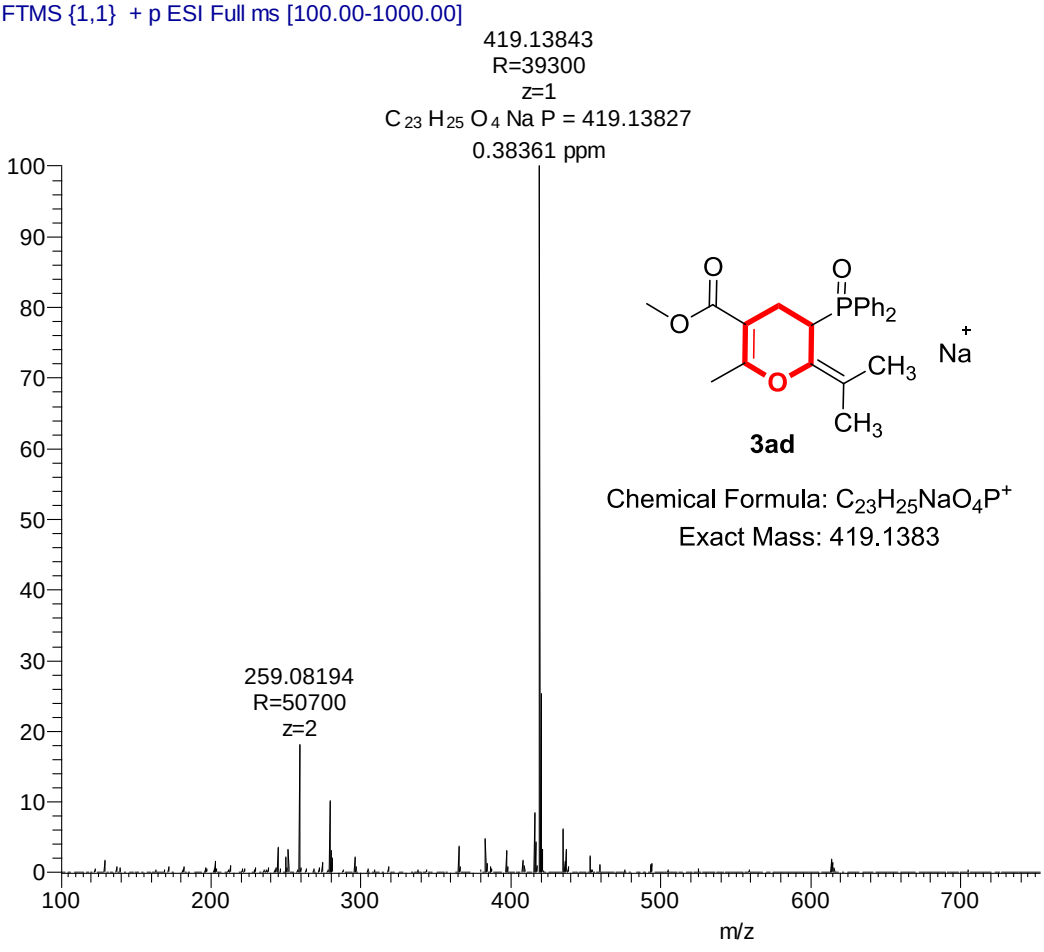


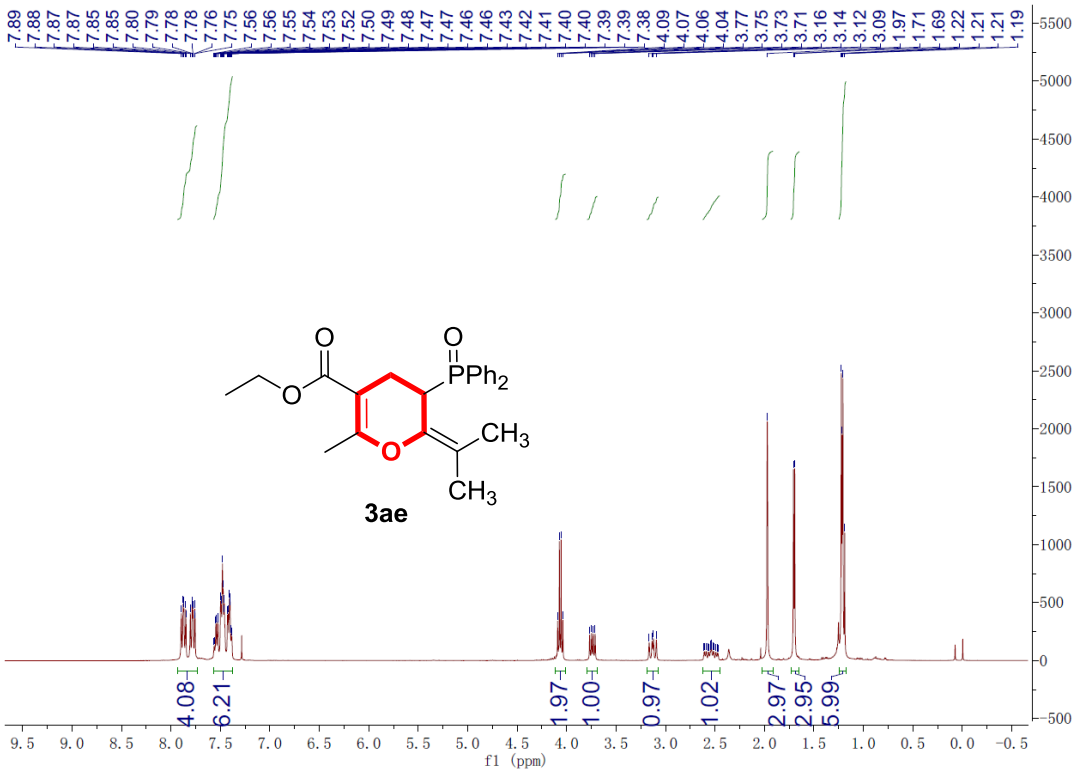

7.88
7.87
7.86
7.86
7.84
7.78
7.76
7.76
7.75
7.73
7.56
7.54
7.53
7.52
7.50
7.49
7.48
7.46
7.46
7.42
7.42
7.40
7.40
7.39
7.38
7.28
3.77
3.75
3.73
3.71
3.60
3.11
3.10
3.07
2.60
2.54
2.53
1.70
1.68
1.21
1.20
O
O
PPh2
O
CH3
CH3
3ad
4.17
6.21
1.10
2.99
1.03
1.11
3.02
3.00
3.01
f1 (ppm)

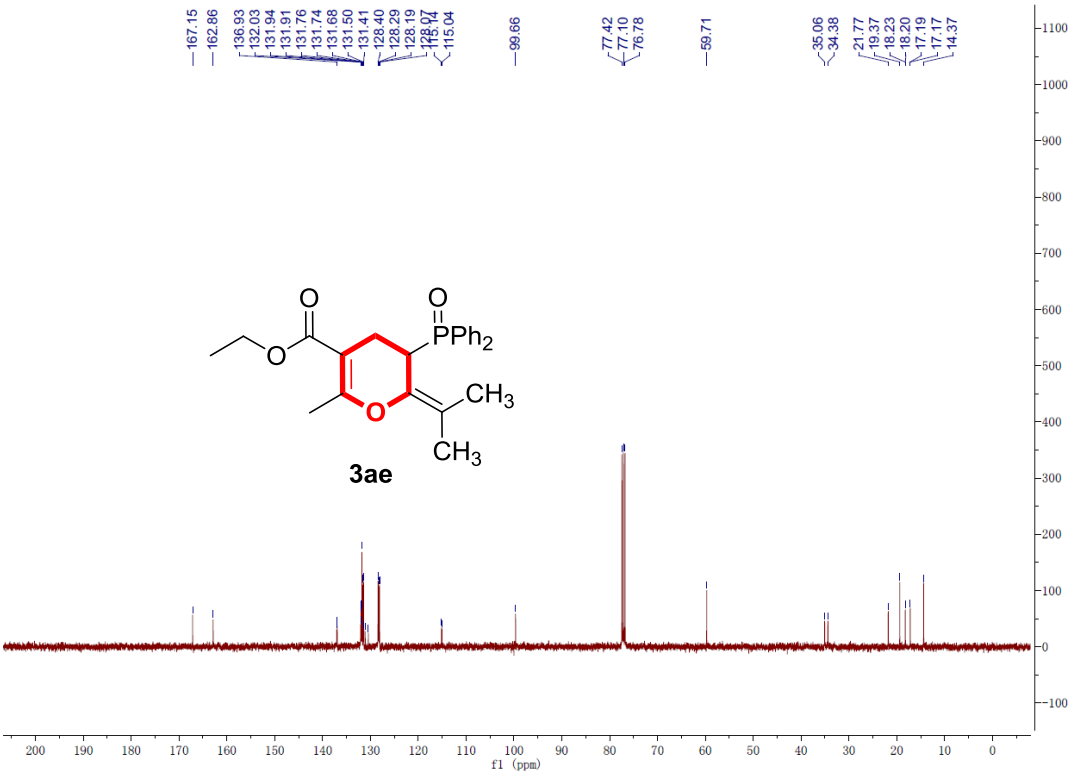

167.58
163.19
136.97
136.88
131.98
131.95
131.80
131.77
131.68
131.53
131.44
128.45
128.34
128.19
128.08
115.25
115.15
99.42
77.37
77.05
76.74
51.08
34.95
34.27
21.76
21.75
19.35
18.24
18.21
17.19
17.17
O
O
PPh2
O
CH3
CH3
3ad
f1 (ppm)

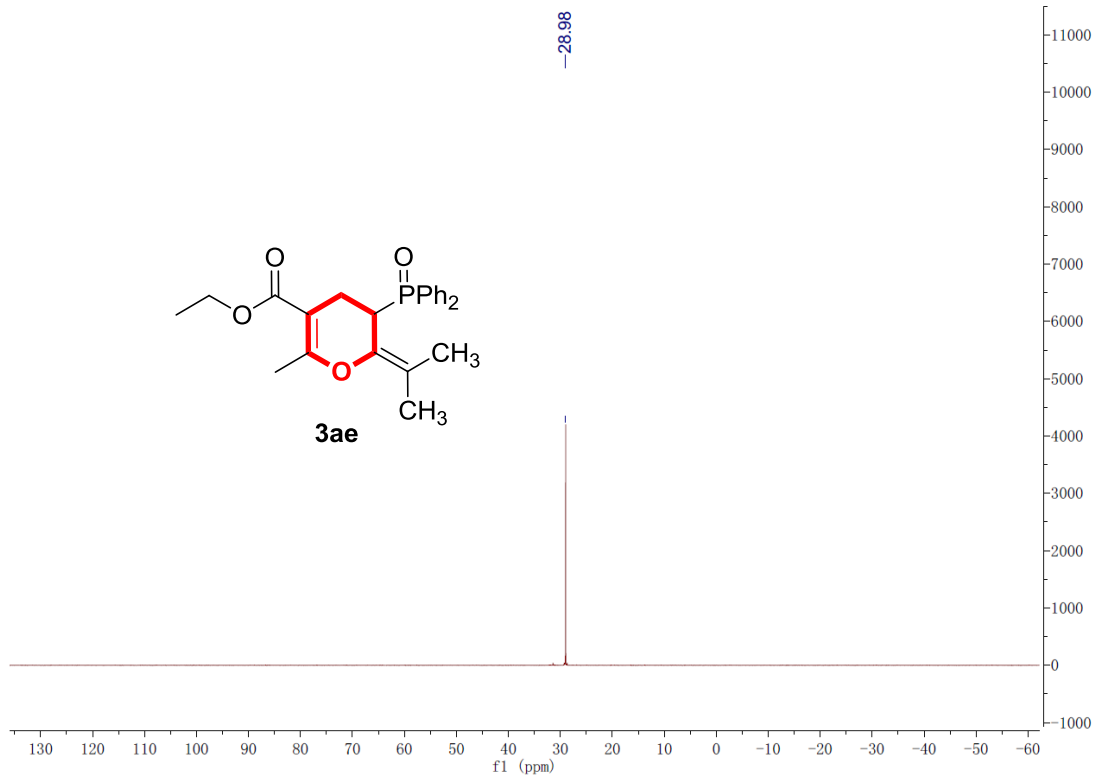


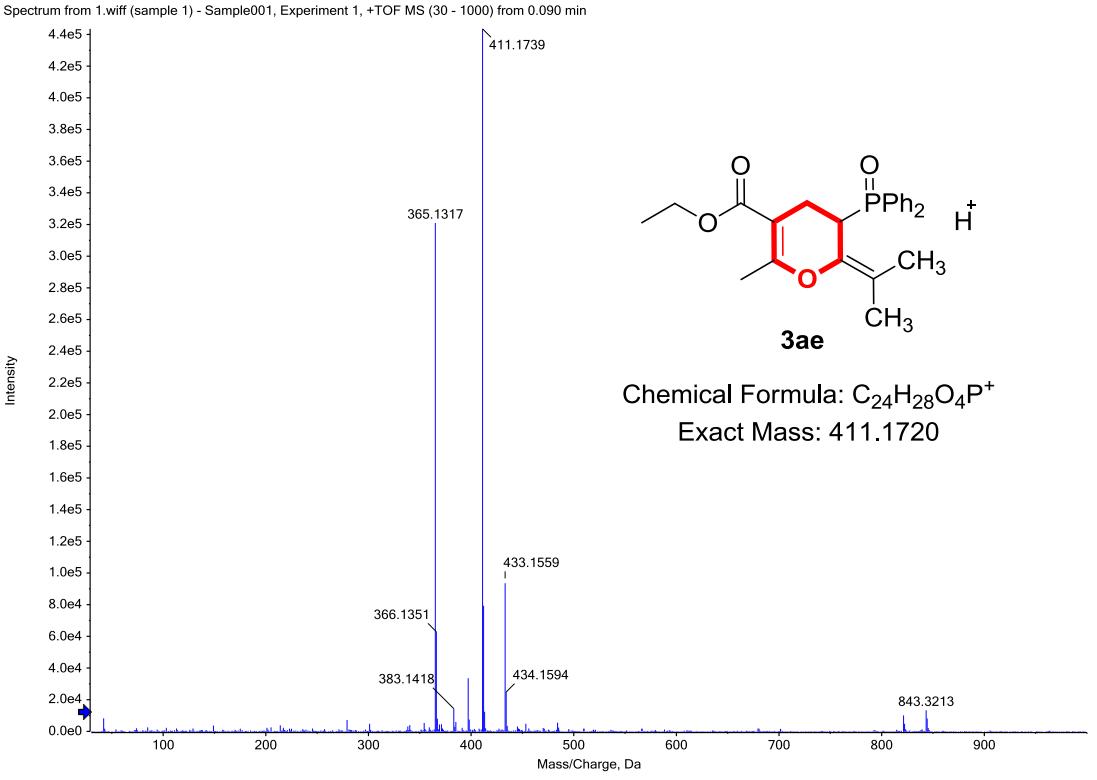

20171228-8 #19 RT: 0.30 AV: 1 NL: 1.01E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

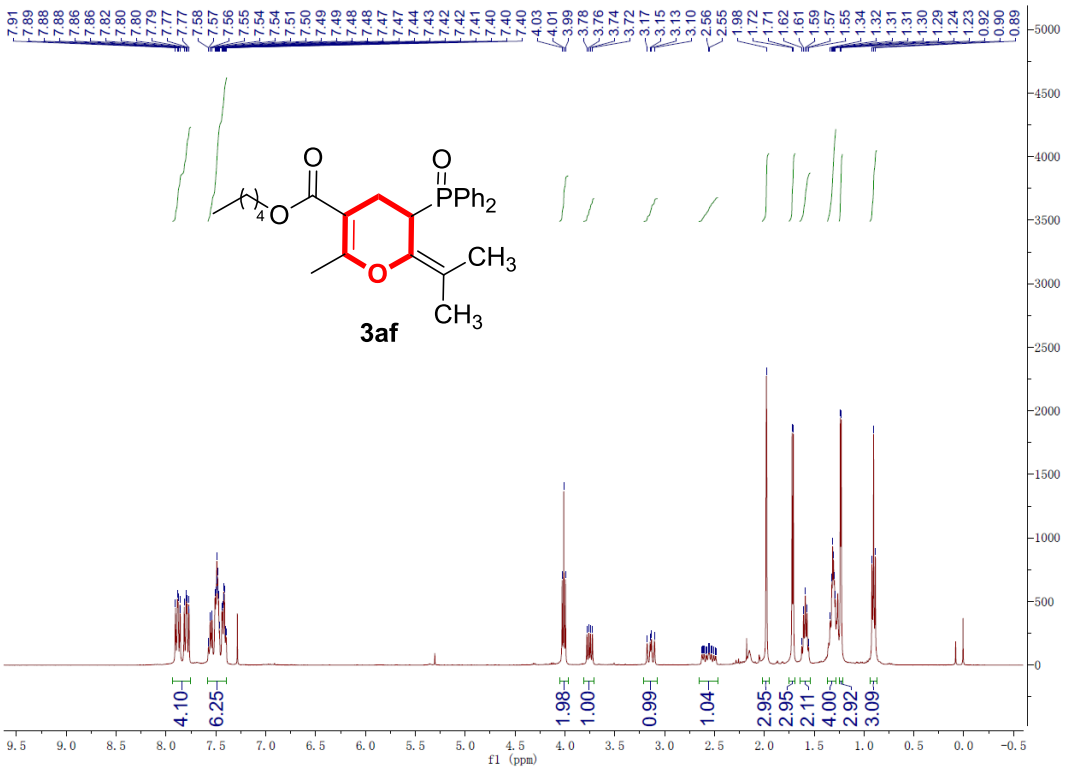


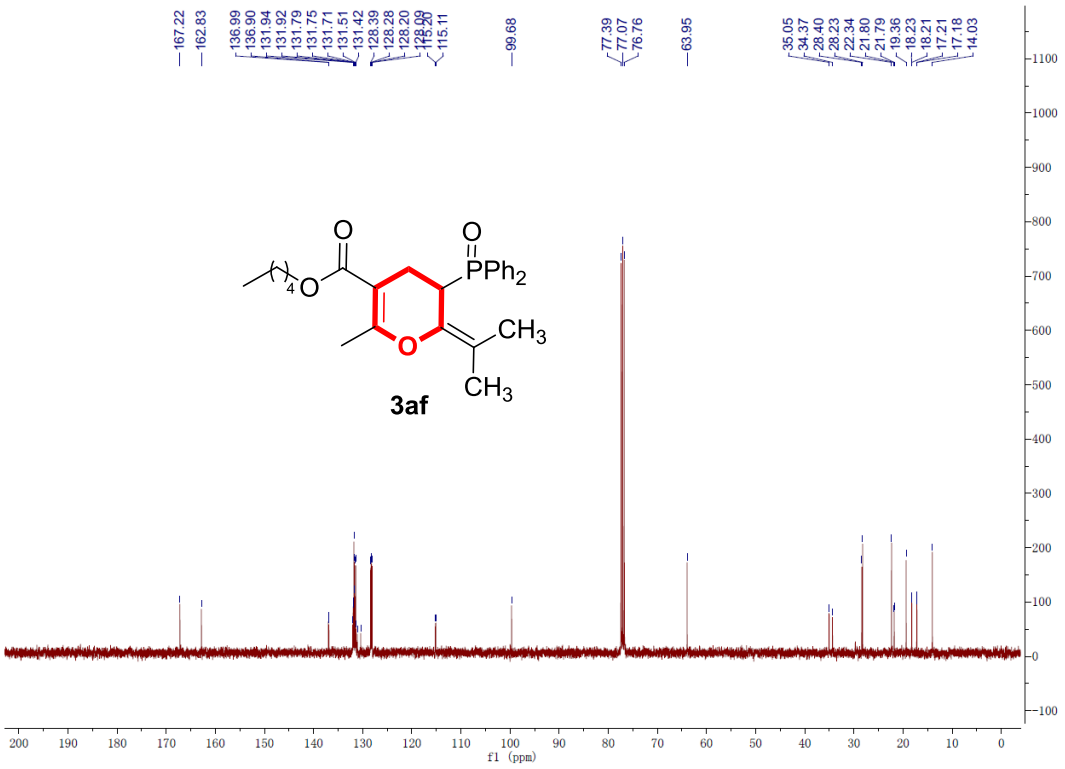

7.89 7.88 7.87 7.87 7.85 7.85 7.80 7.79 7.78 7.78 7.76 7.75 7.56 7.56 7.55 7.54 7.53 7.52 7.50 7.49 7.48 7.47 7.47 7.46 7.46 7.43 7.42 7.41 7.40 7.40 7.39 7.39 7.38 4.09 4.07 4.06 4.04 3.77 3.75 3.73 3.71 3.16 3.14 3.12 3.09 1.97 1.71 1.69 1.22 1.21 1.21 1.19
O
O
PPh2
O
CH3
CH3
3ae
4.08
6.21
1.97
1.00
0.97
1.02
2.97
2.95
5.99
f1 (ppm)

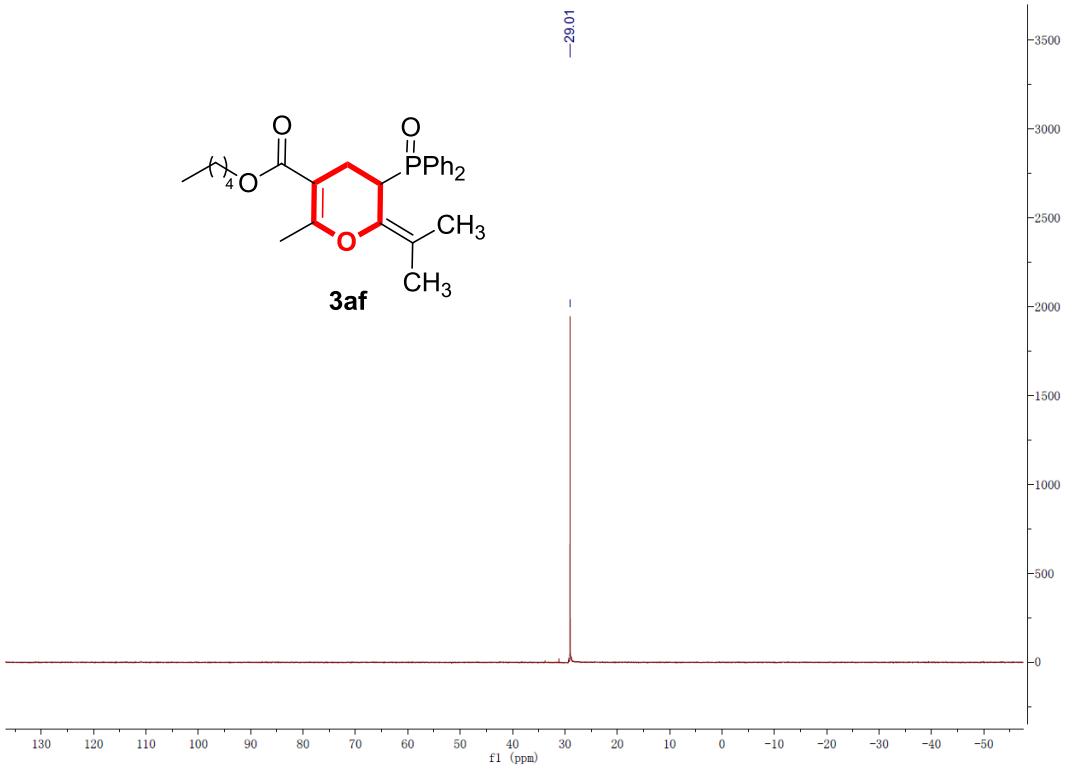

167.15 162.86 136.93 132.03 131.94 131.91 131.76 131.74 131.68 131.50 131.41 128.40 128.29 128.19 115.04
99.66
77.42 77.10 76.78
59.71
35.06 34.38
21.77 19.37 18.23 18.20 17.19 17.17 14.37
O
O
PPh2
O
CH3
CH3
3ae
f1 (ppm)


28.98
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)
O
O
PPh2
O
CH3
CH3
3ae

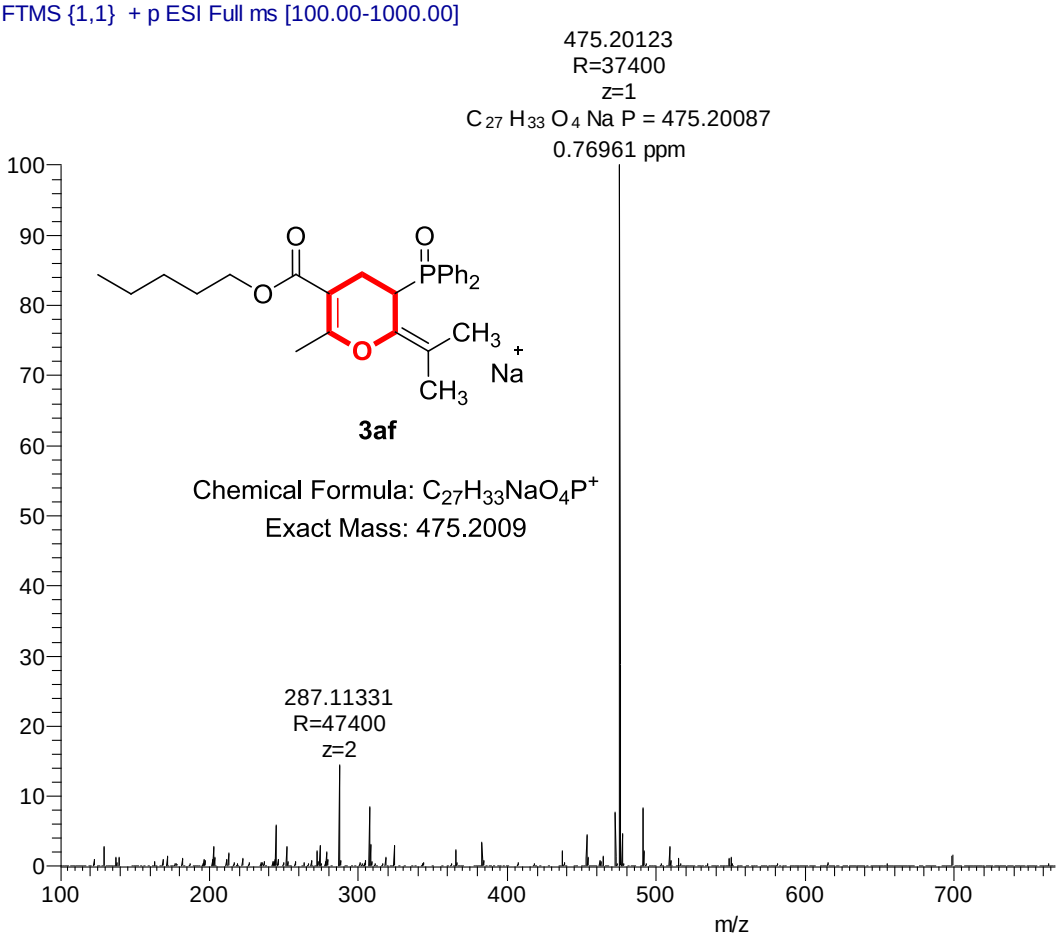

Spectrum from 1.wiff (sample 1) - Sample001, Experiment 1, +TOF MS (30 - 1000) from 0.090 min
Intensity
4.4e5
4.2e5
4.0e5
3.8e5
3.6e5
3.4e5
3.2e5
3.0e5
2.8e5
2.6e5
2.4e5
2.2e5
2.0e5
1.8e5
1.6e5
1.4e5
1.2e5
1.0e5
8.0e4
6.0e4
4.0e4
2.0e4
0.0e0
411.1739
365.1317
433.1559
366.1351
383.1418
434.1594
843.3213
100 200 300 400 500 600 700 800 900
Mass/Charge, Da
O
O
PPh2
H+
O
CH3
CH3
3ae
Chemical Formula: C24H28O4P+
Exact Mass: 411.1720

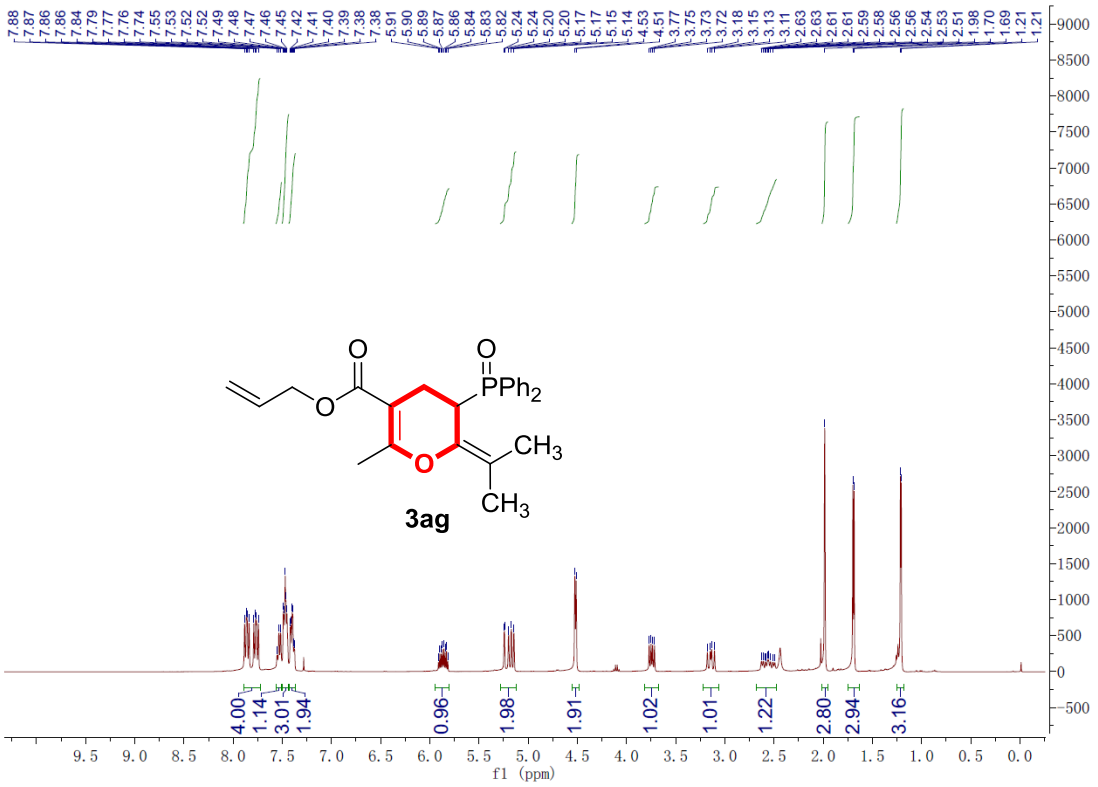

3af
4.10
6.25
1.98
1.00
0.99
1.04
2.95
2.95
2.11
4.00
2.92
3.09
f1 (ppm)

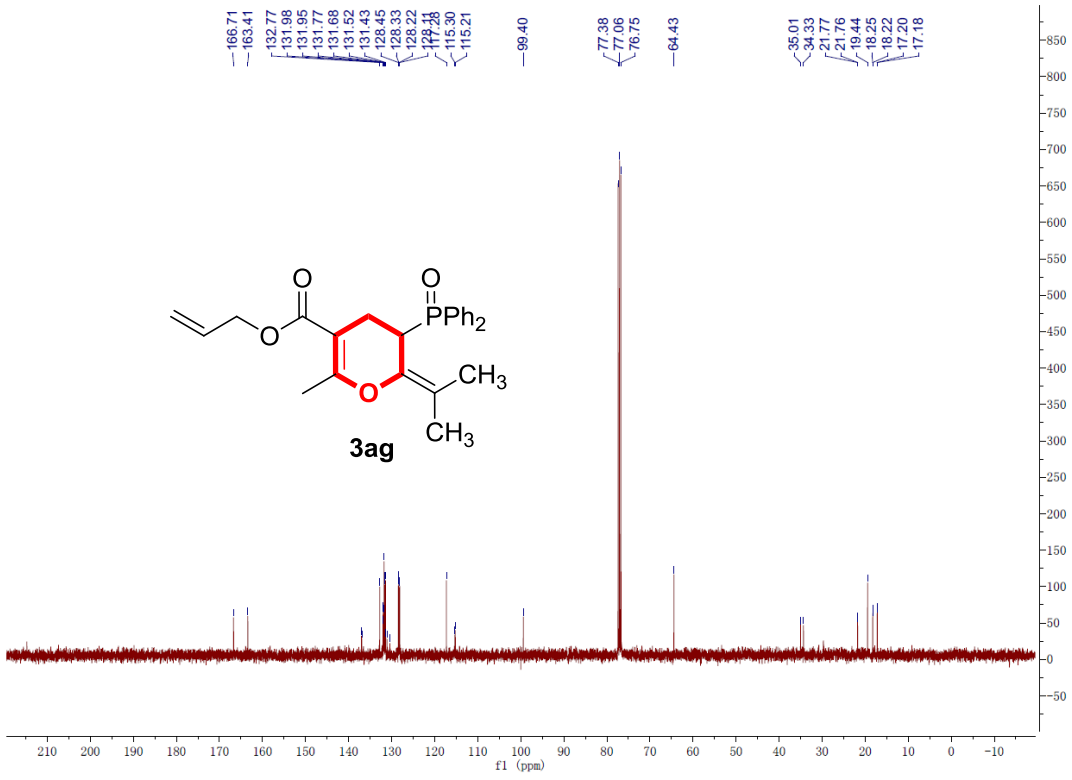

3af
f1 (ppm)

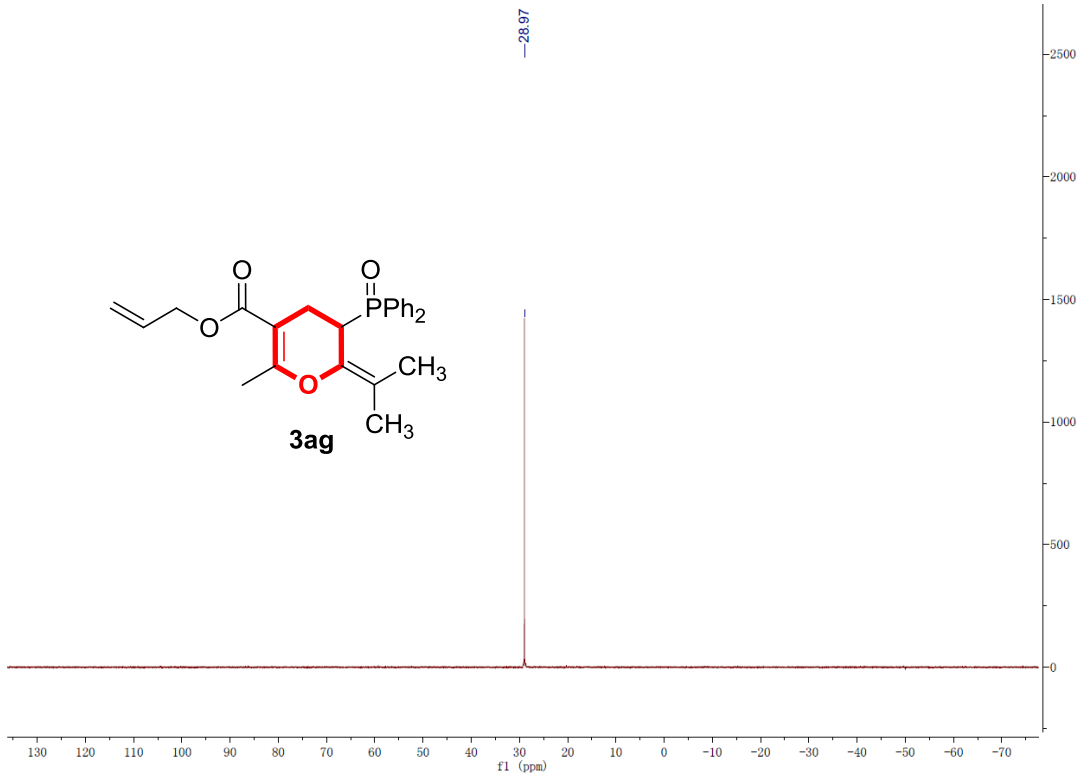



20171228-13 #23 RT: 0.36 AV: 1 NL: 6.17E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

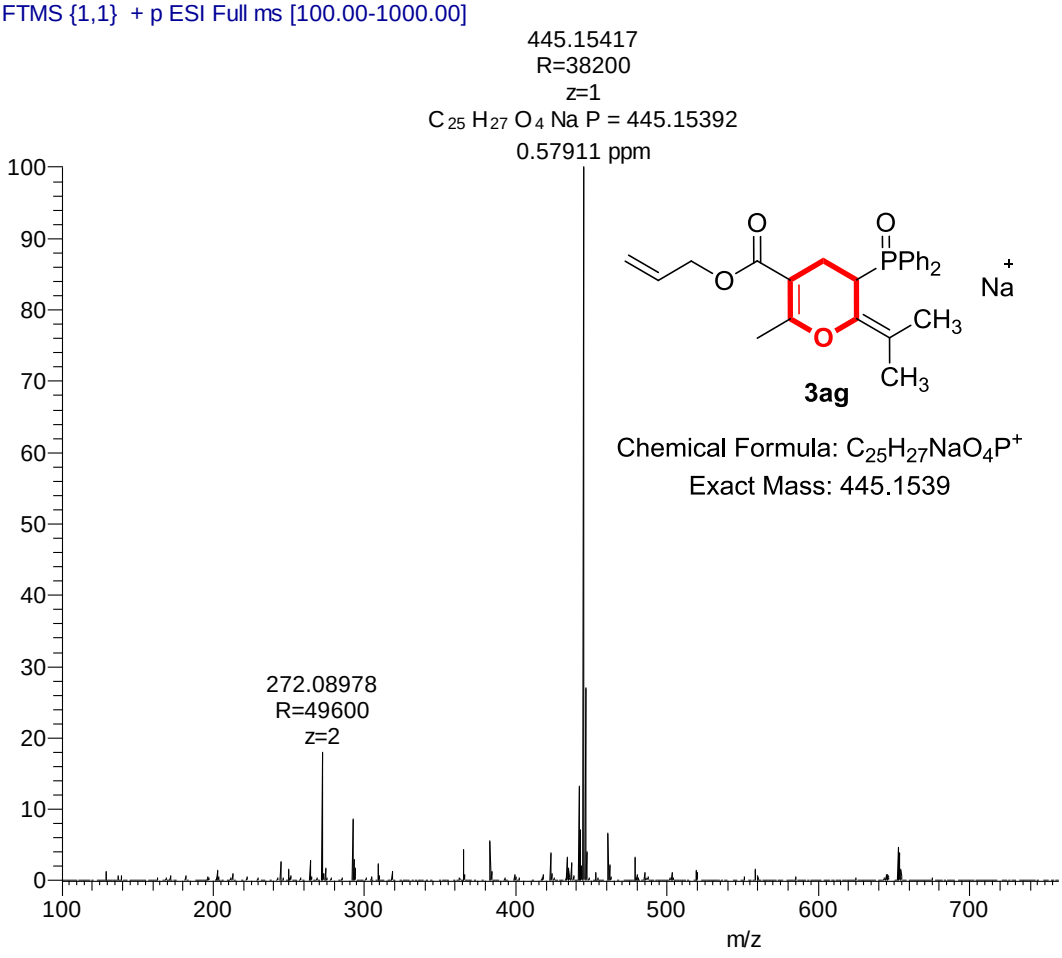


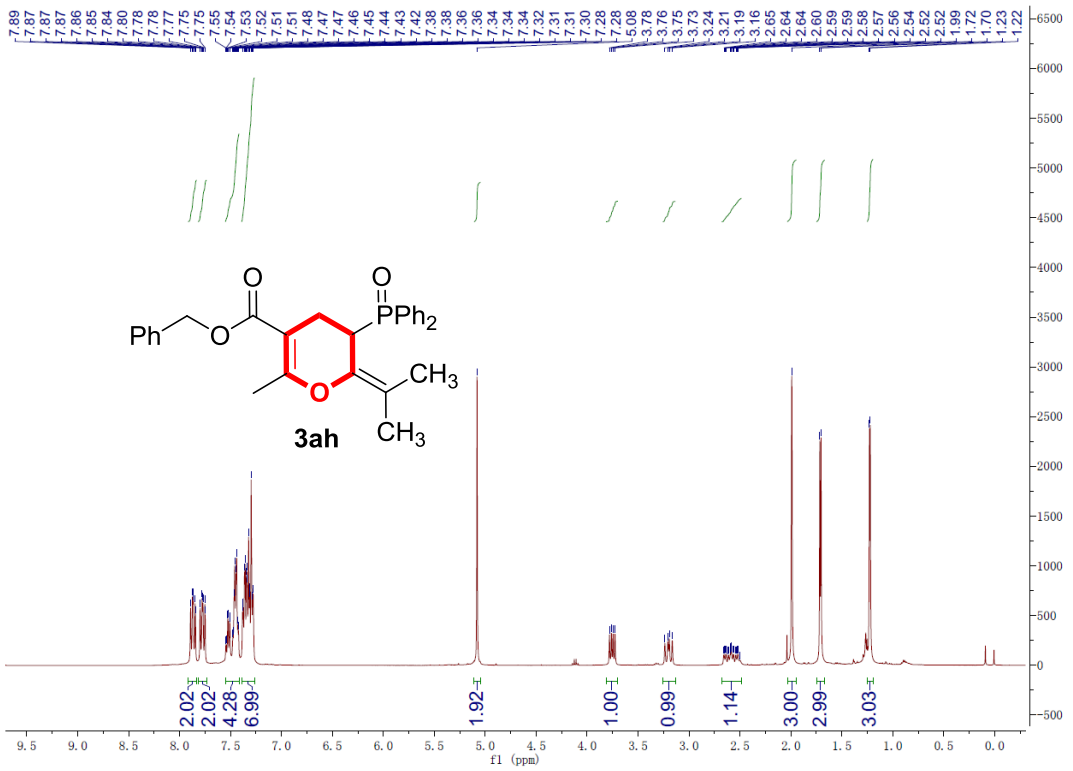

3ag
4.00
1.14
3.01
1.94
0.96
1.98
1.91
1.02
1.01
1.22
2.80
2.94
3.16
f1 (ppm)

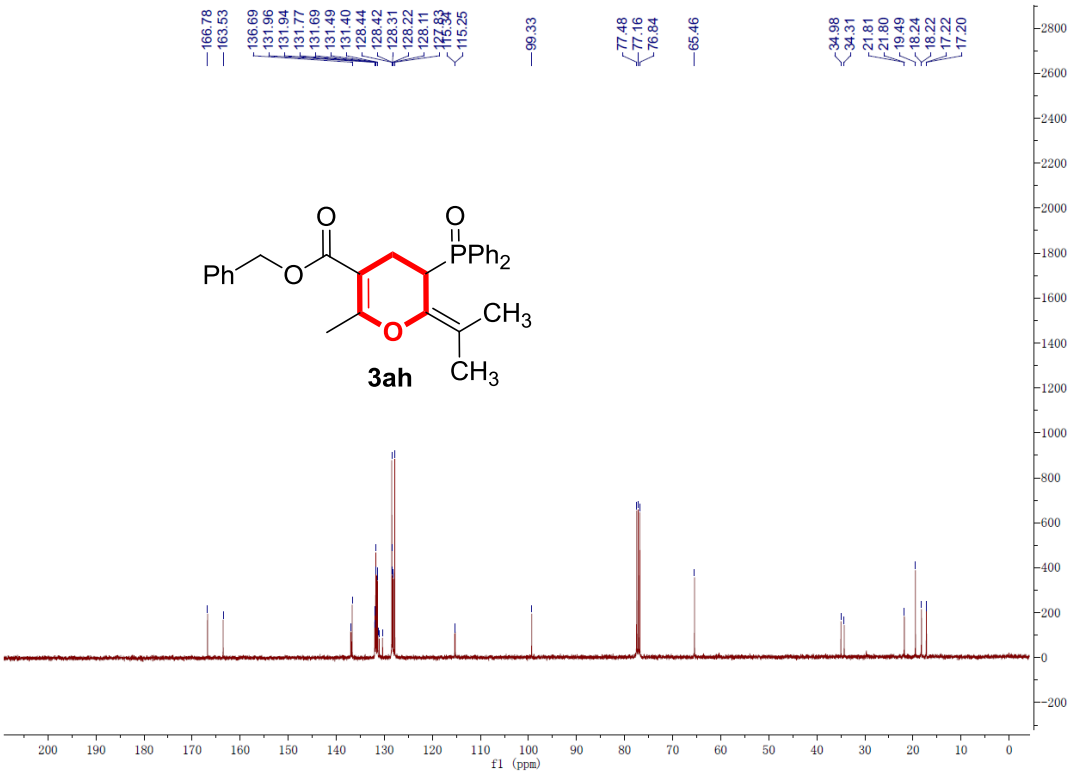

3ag
f1 (ppm)

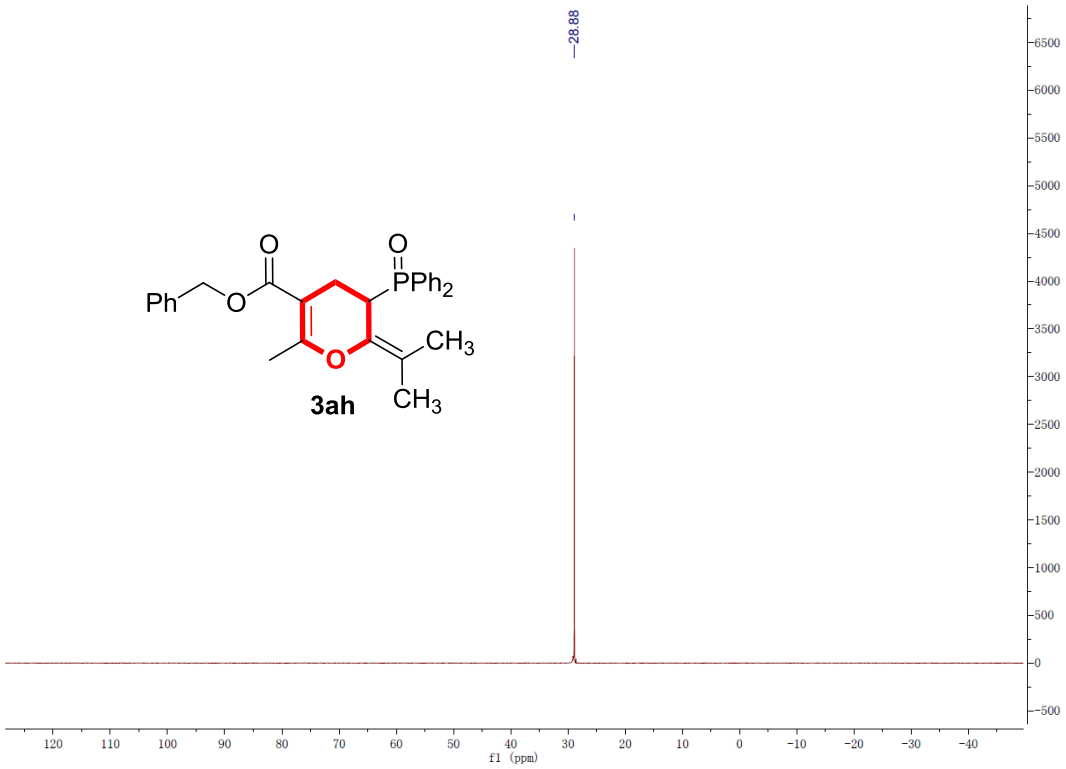



20171228-10 #25 RT: 0.38 AV: 1 NL: 1.15E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

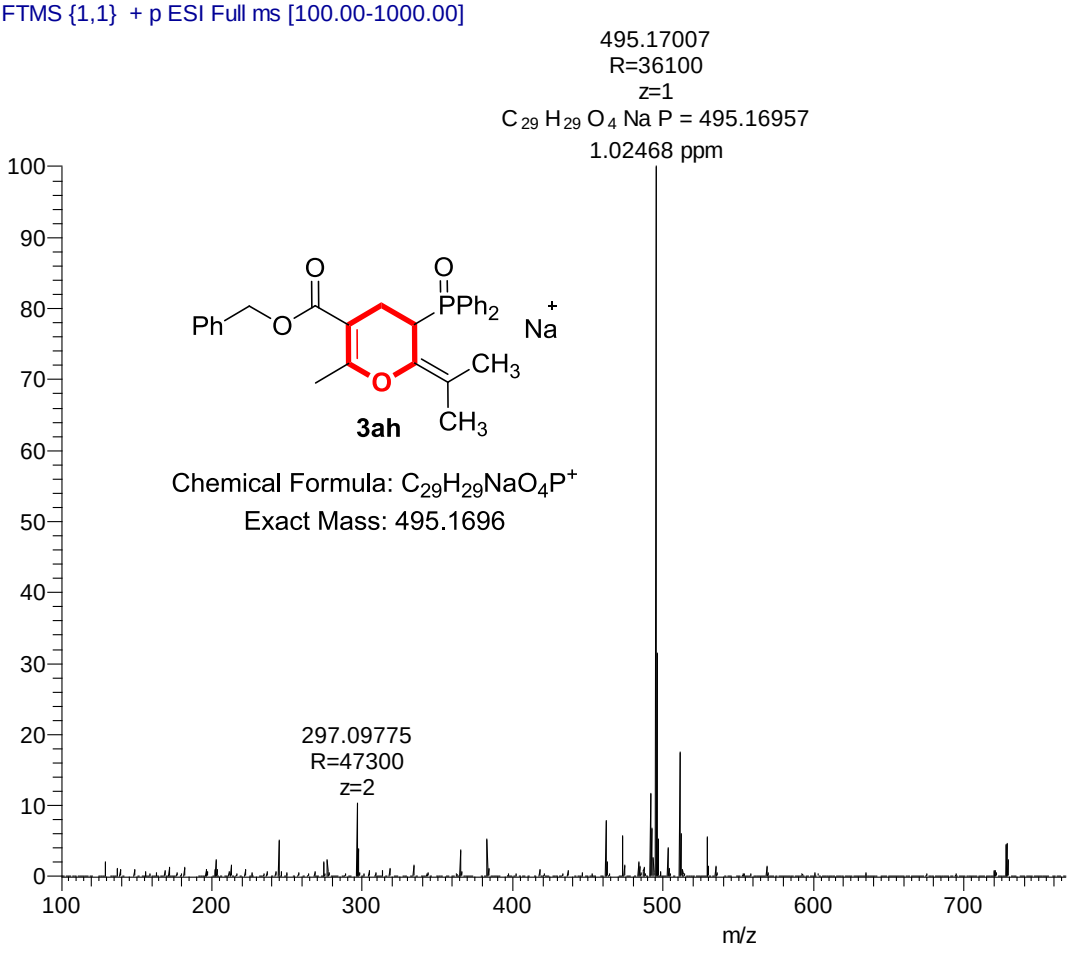


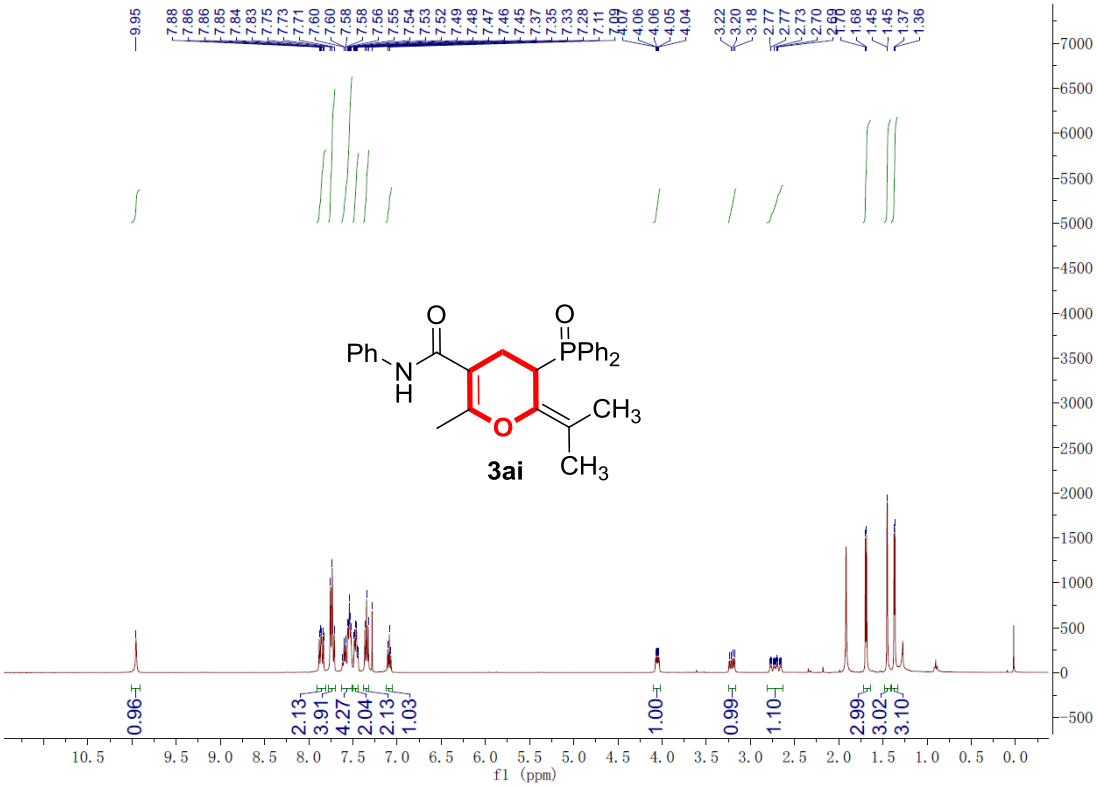

Ph
O
O
O
PPh2
CH3
CH3
3ah
2.02
2.02
4.28
6.99
1.92
1.00
0.99
1.14
3.00
2.99
3.03
f1 (ppm)

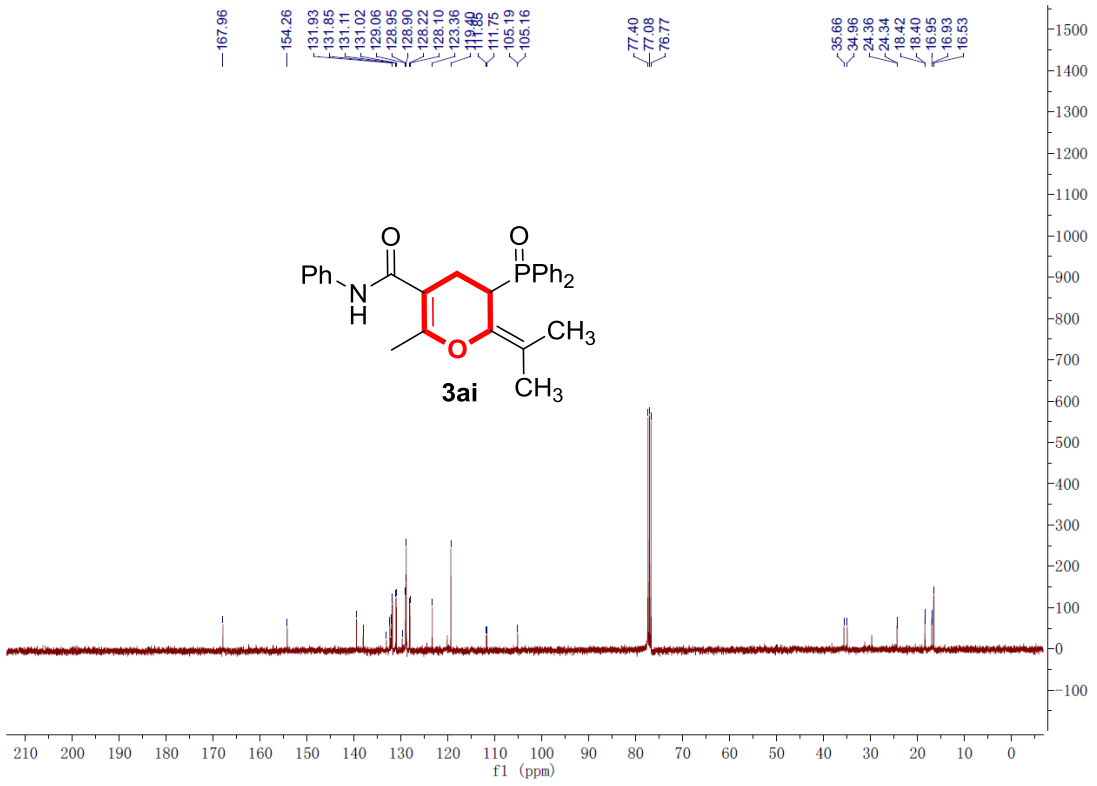

Ph
O
O
O
PPh2
CH3
CH3
3ah
f1 (ppm)

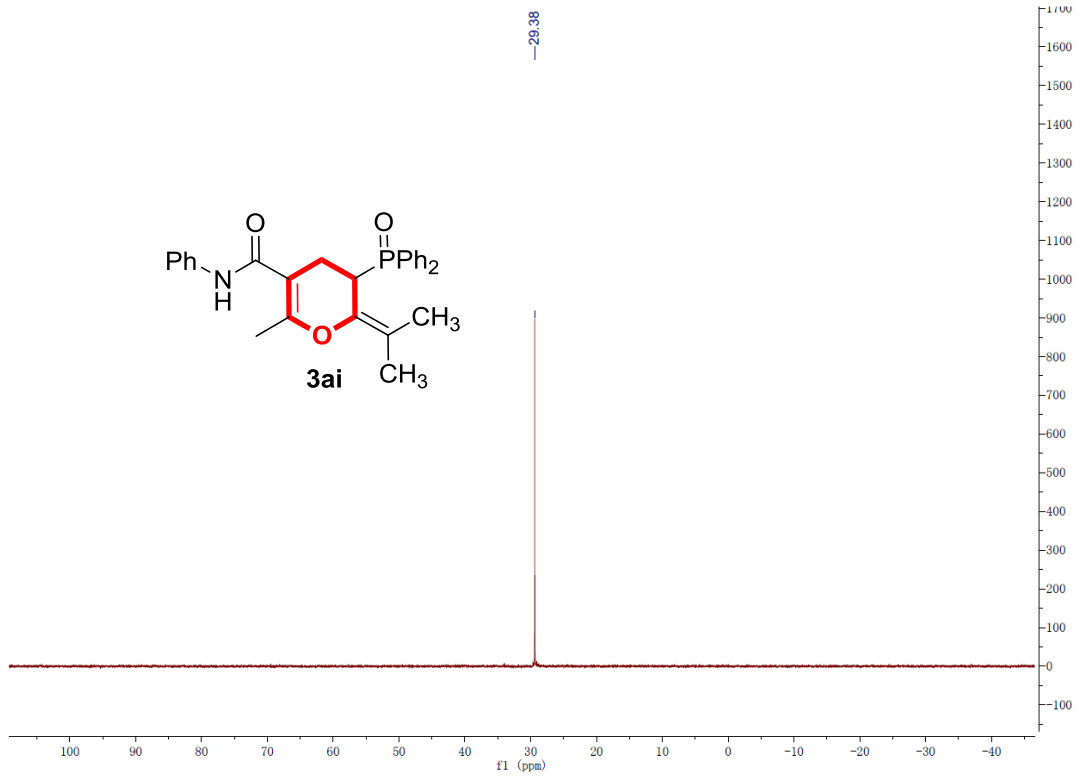



20171228-11 #23 RT: 0.36 AV: 1 NL: 6.49E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

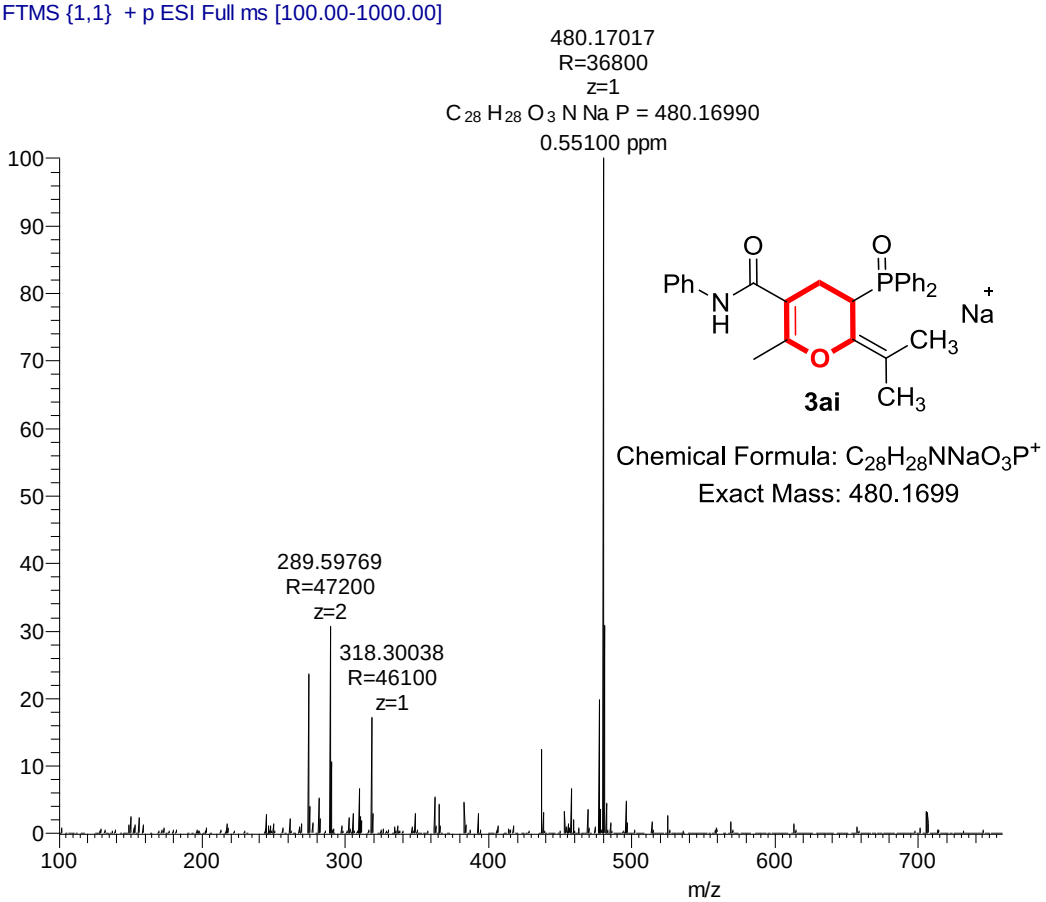


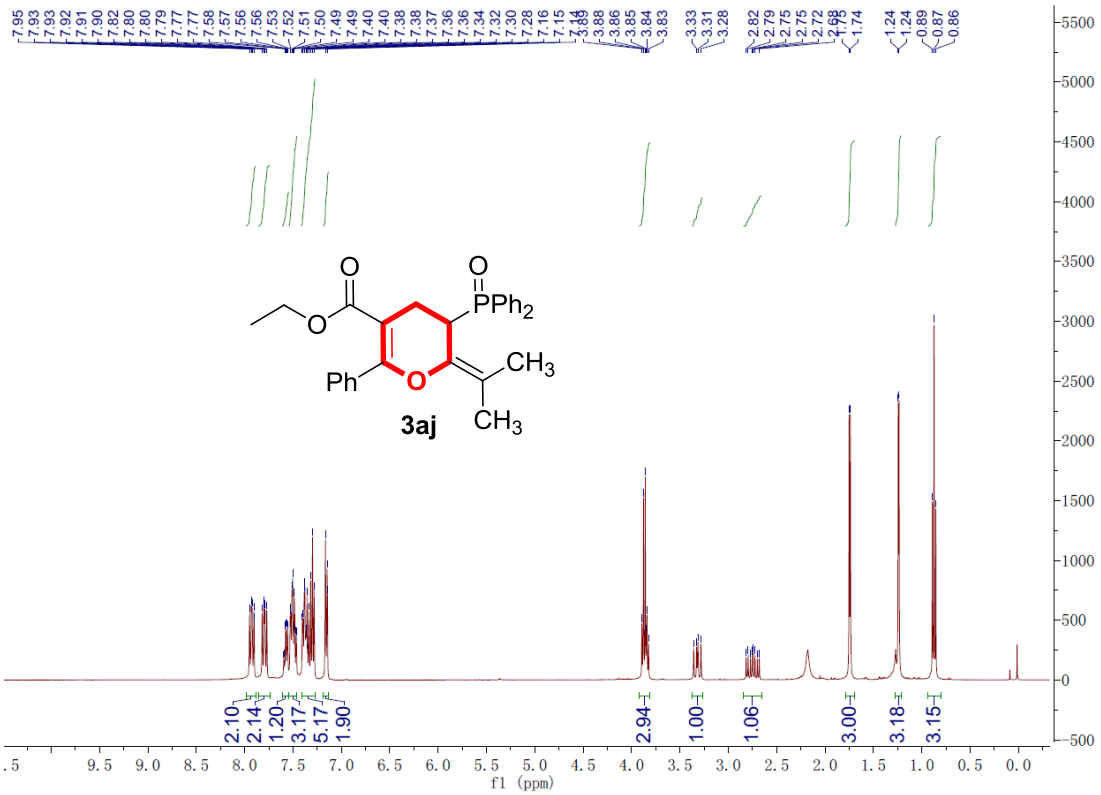

3ai
f1 (ppm)

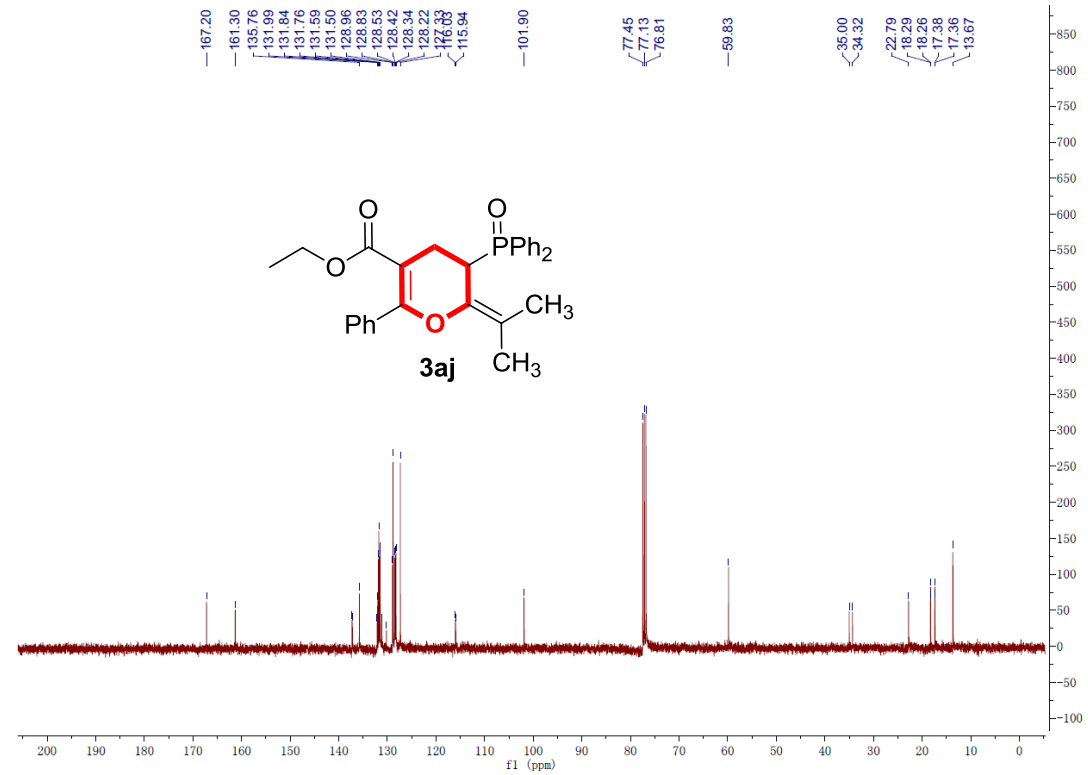

3ai
f1 (ppm)

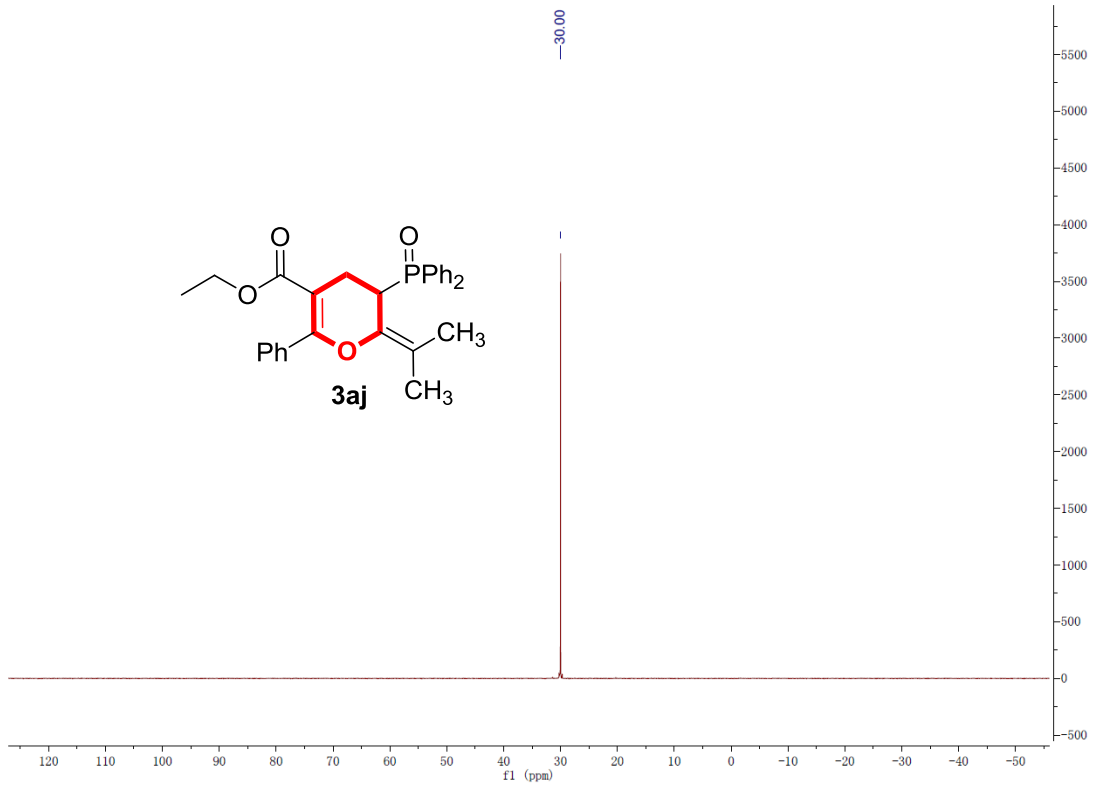



20171228-12 #13 RT: 0.21 AV: 1 NL: 1.52E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

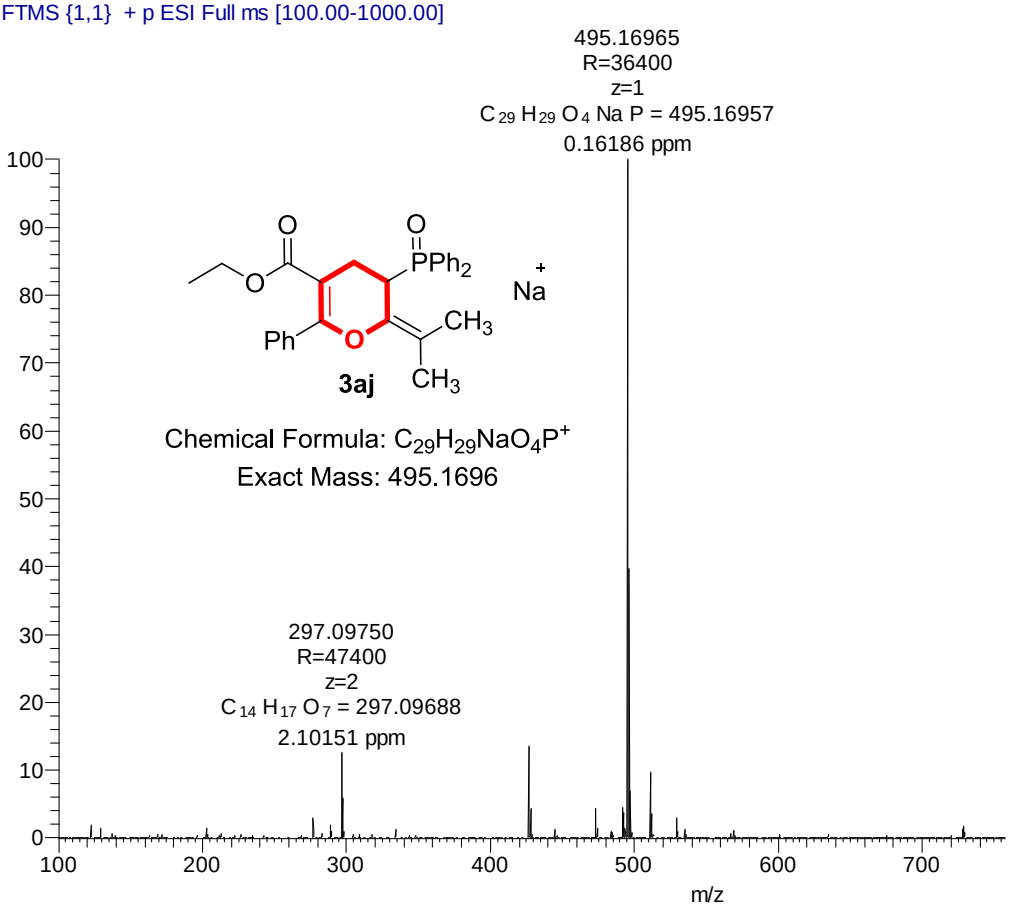


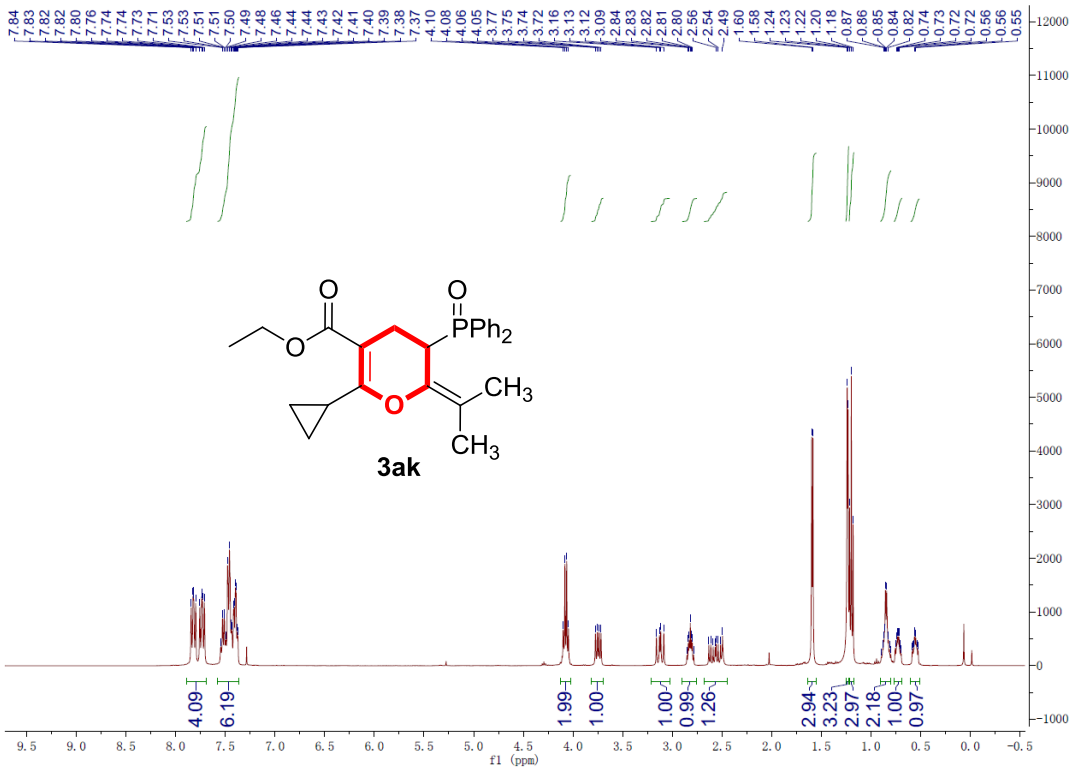

3aj
f1 (ppm)

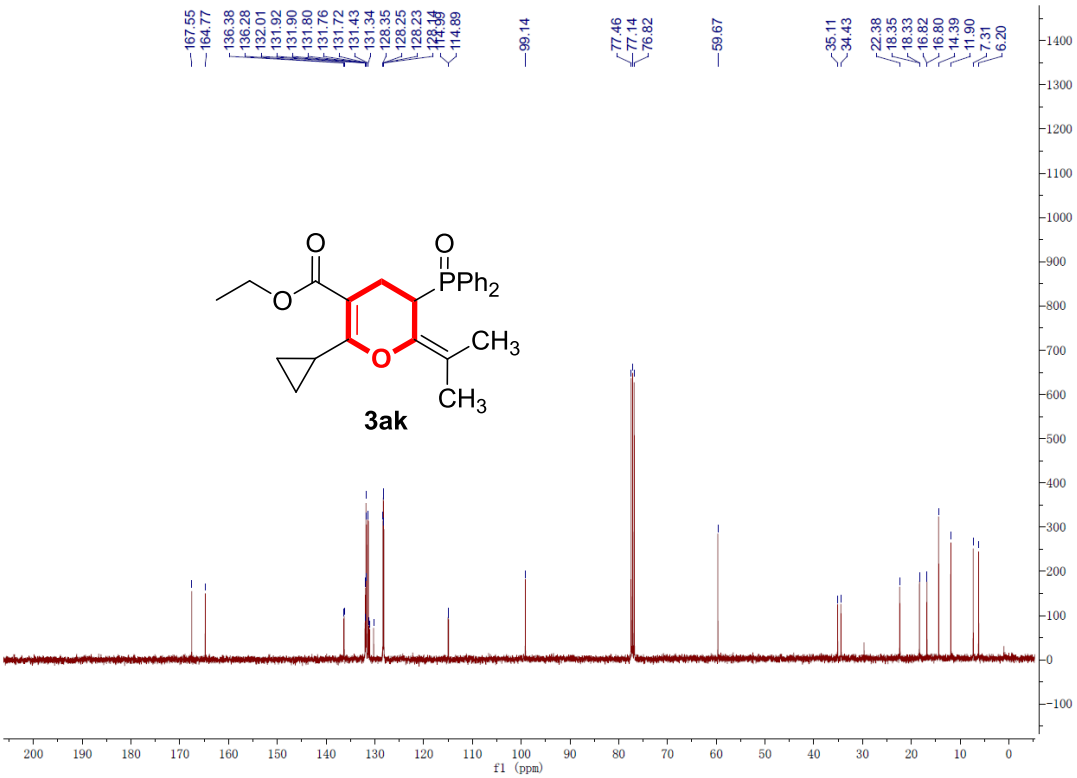

3aj
f1 (ppm)

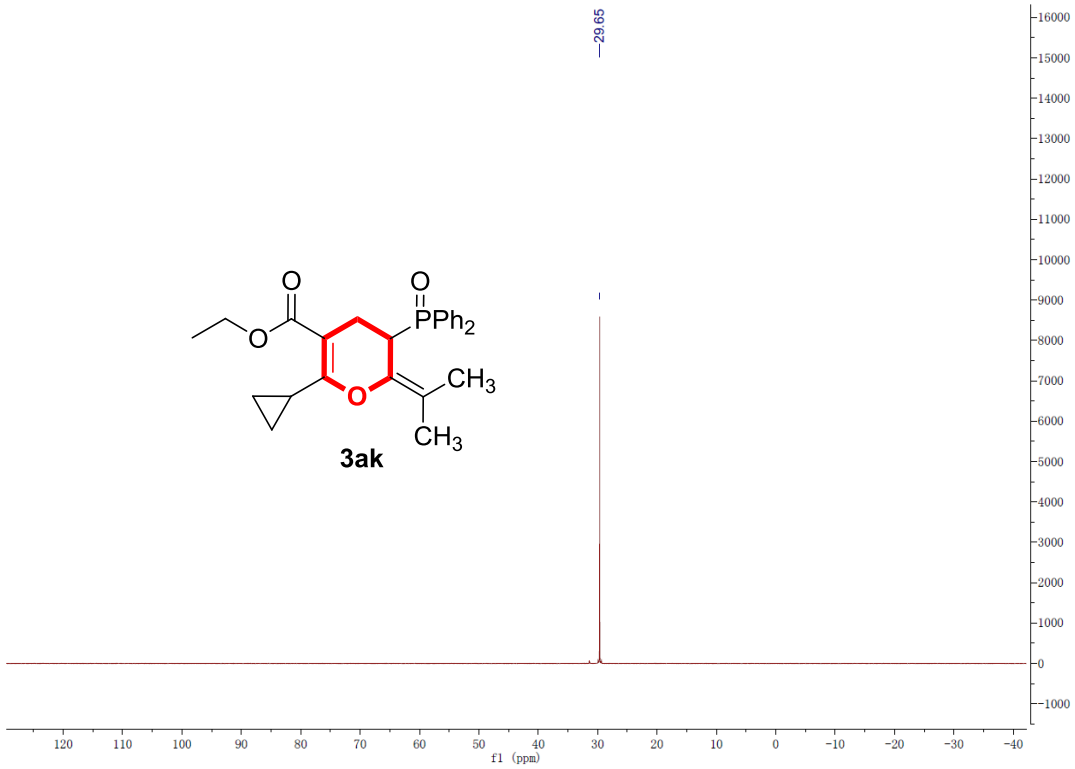



20180104-38 #29 RT: 0.43 AV: 1 NL: 1.78E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

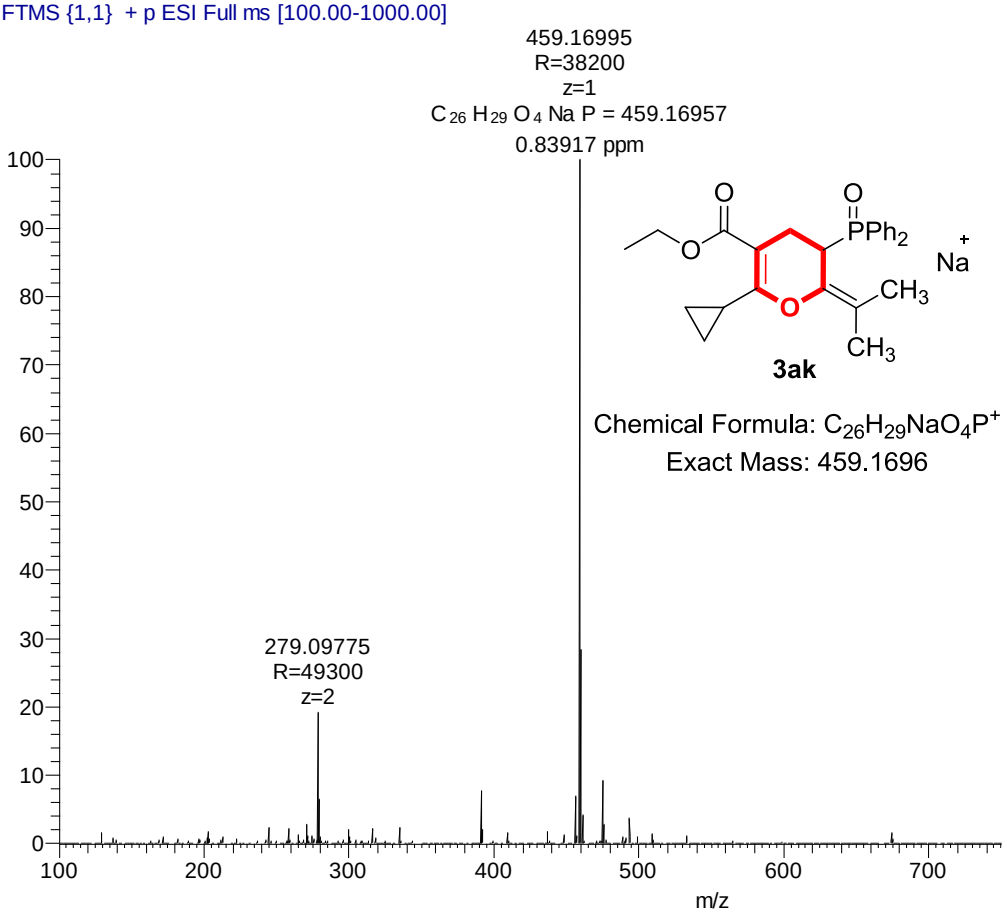


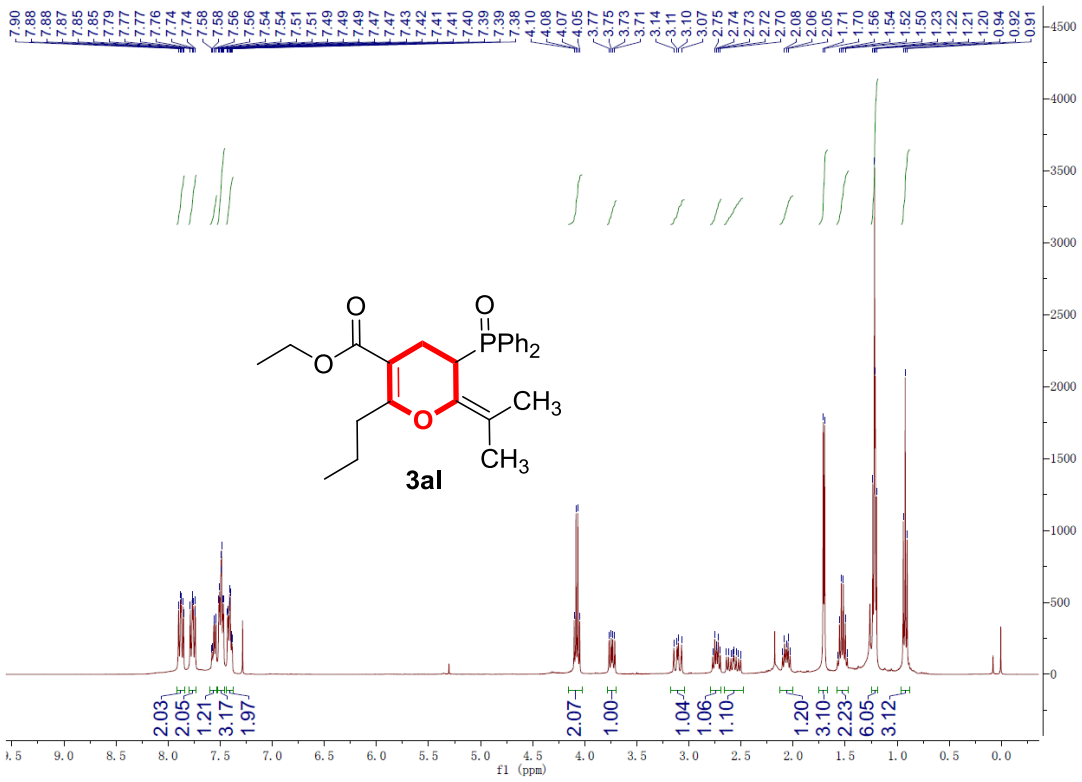

3ak
f1 (ppm)

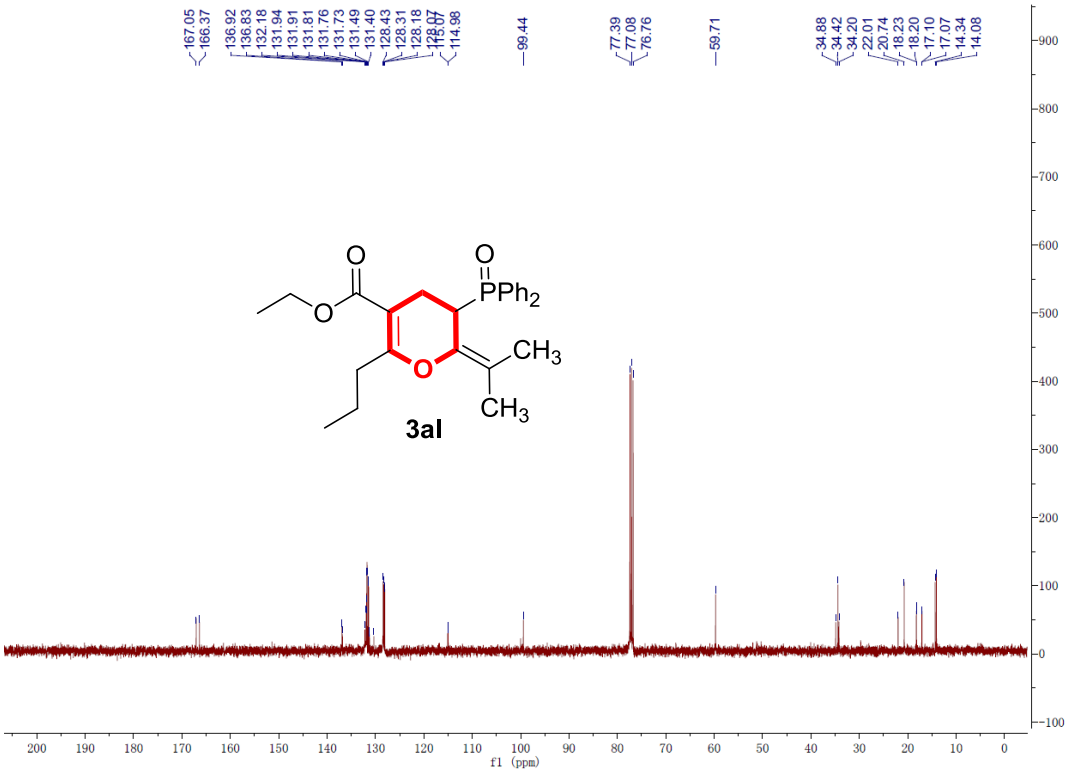

3ak
f1 (ppm)

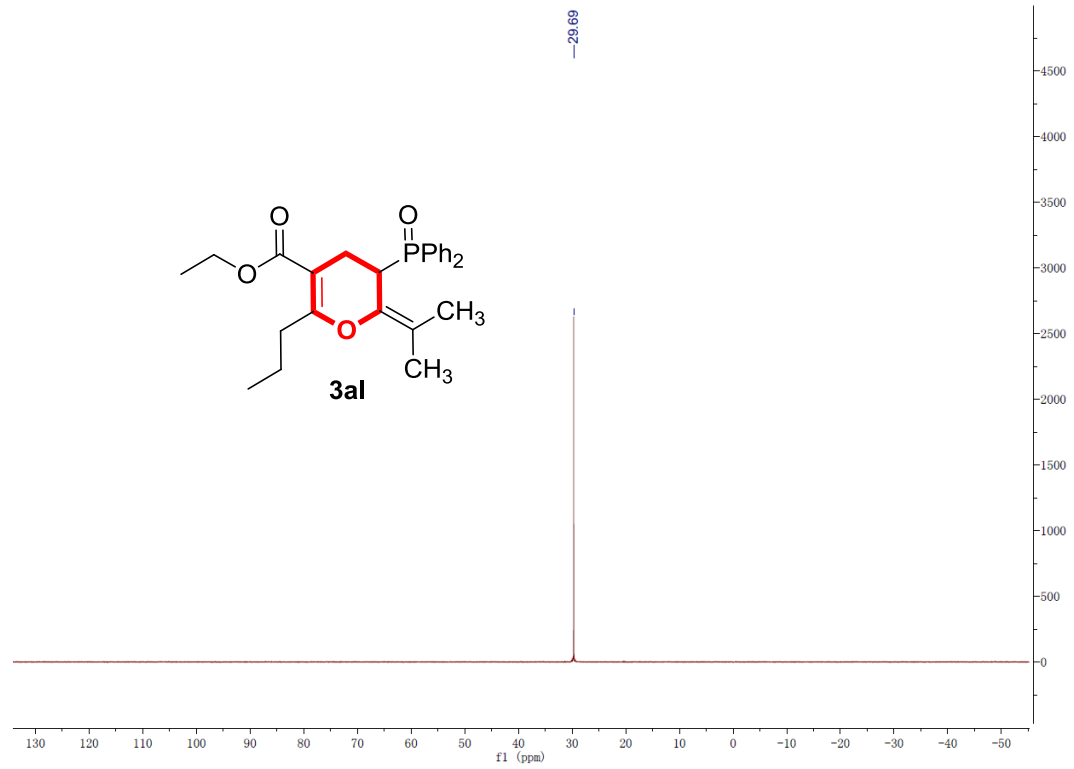



20171228-14 #23 RT: 0.35 AV: 1 NL: 9.02E5
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

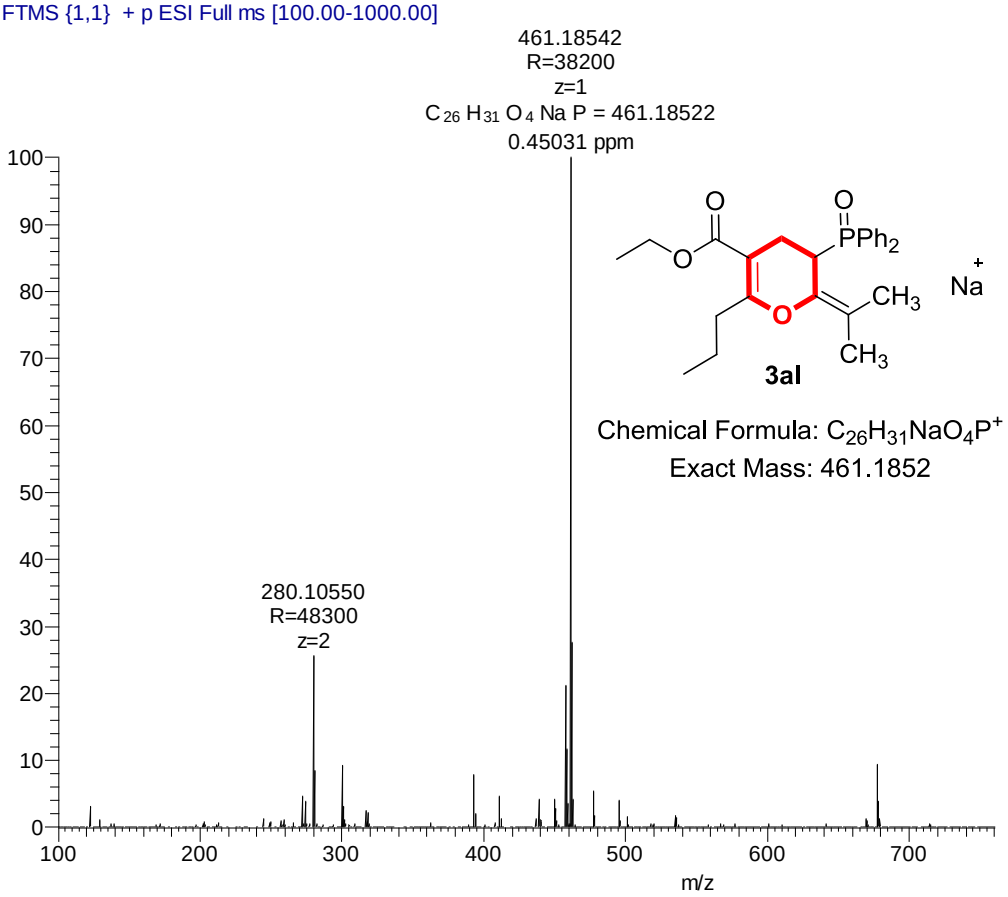


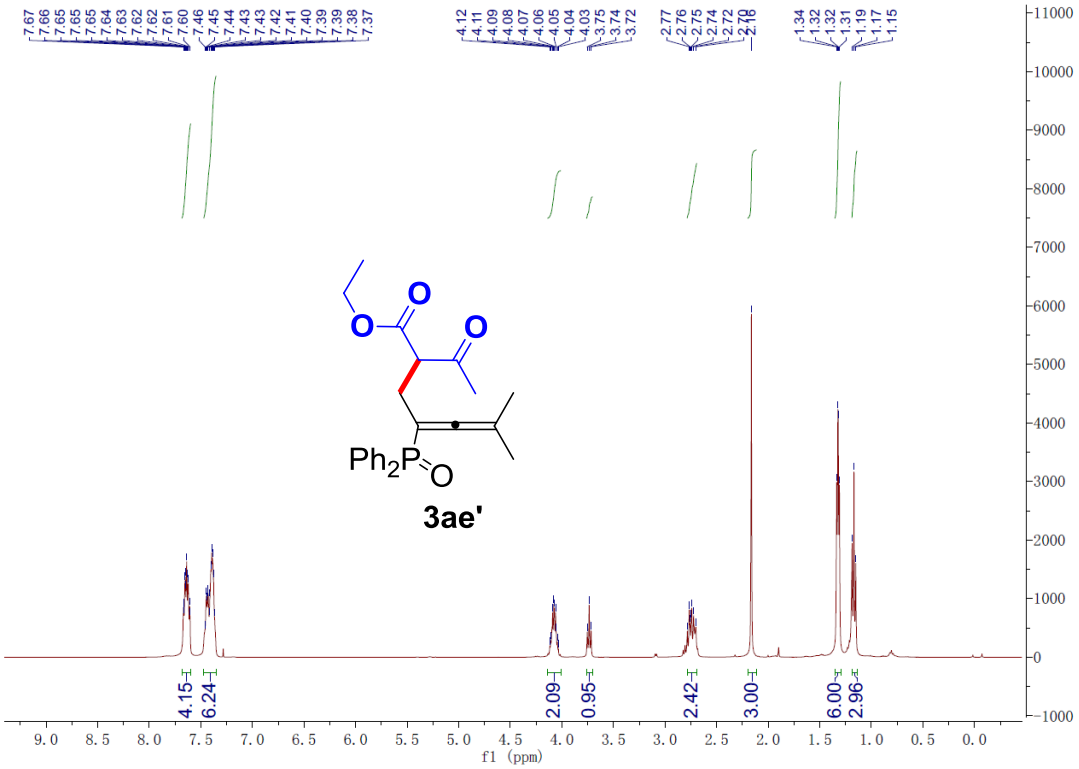

O
O
PPh2
CH3
O
CH3
3al
f1 (ppm)

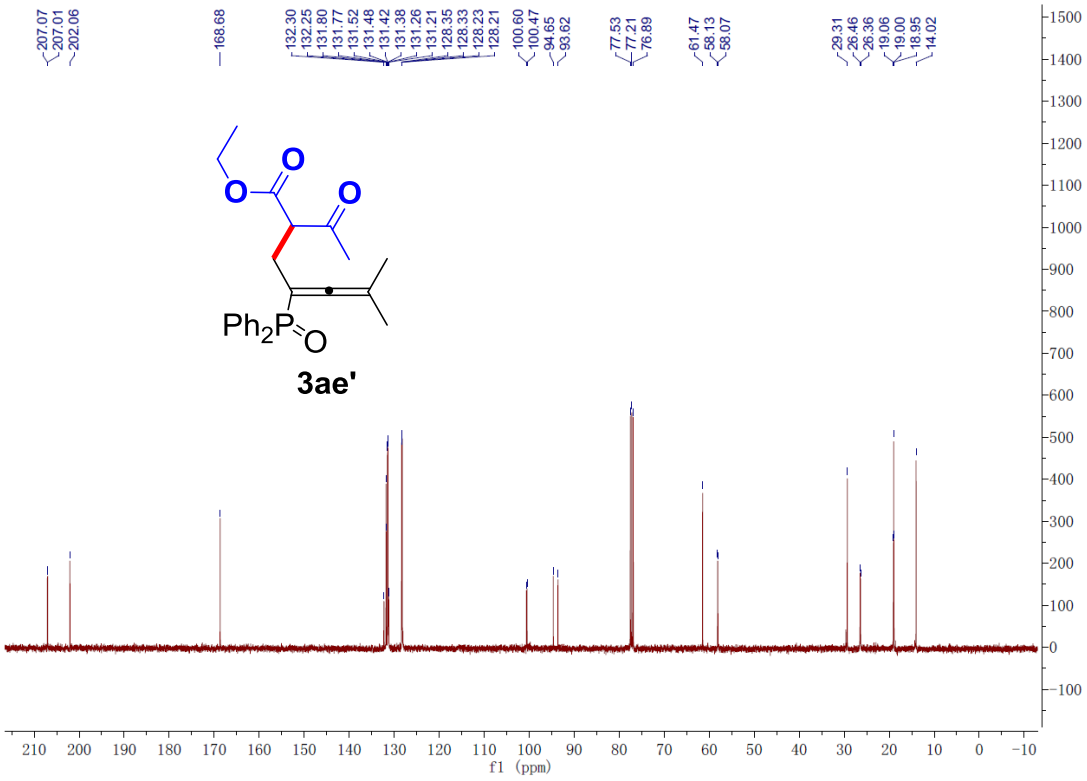

O
O
PPh2
CH3
O
CH3
3al
f1 (ppm)

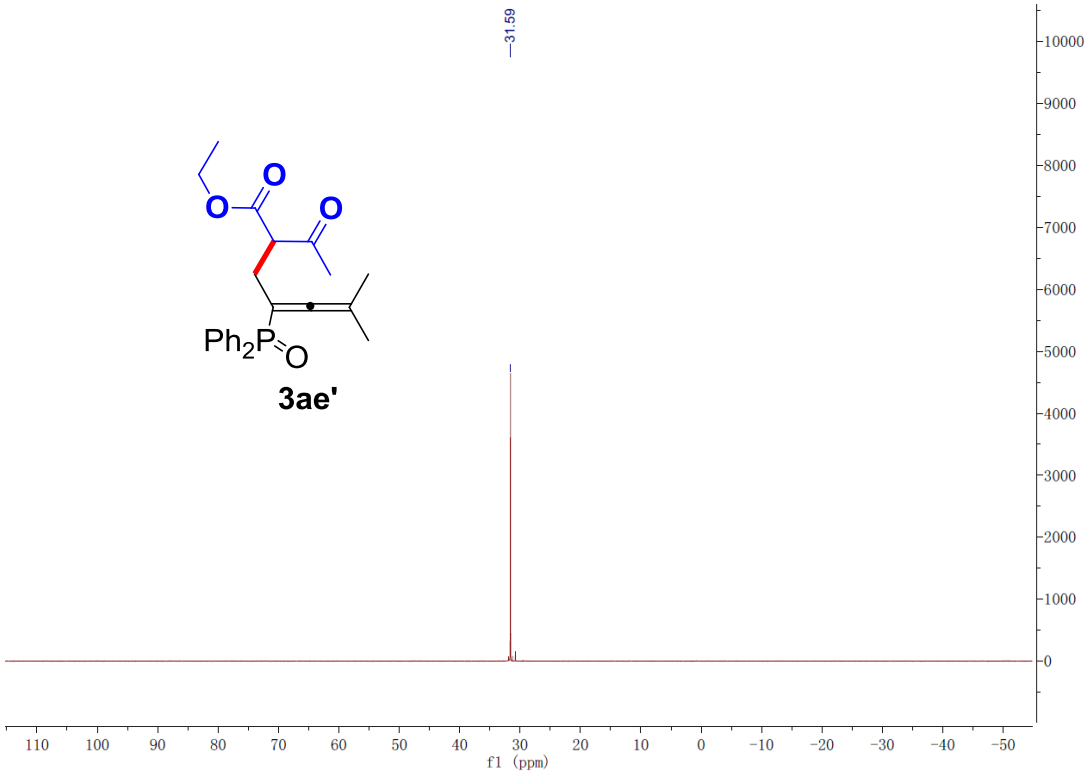



20171228-16 #19 RT: 0.30 AV: 1 NL: 1.15E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

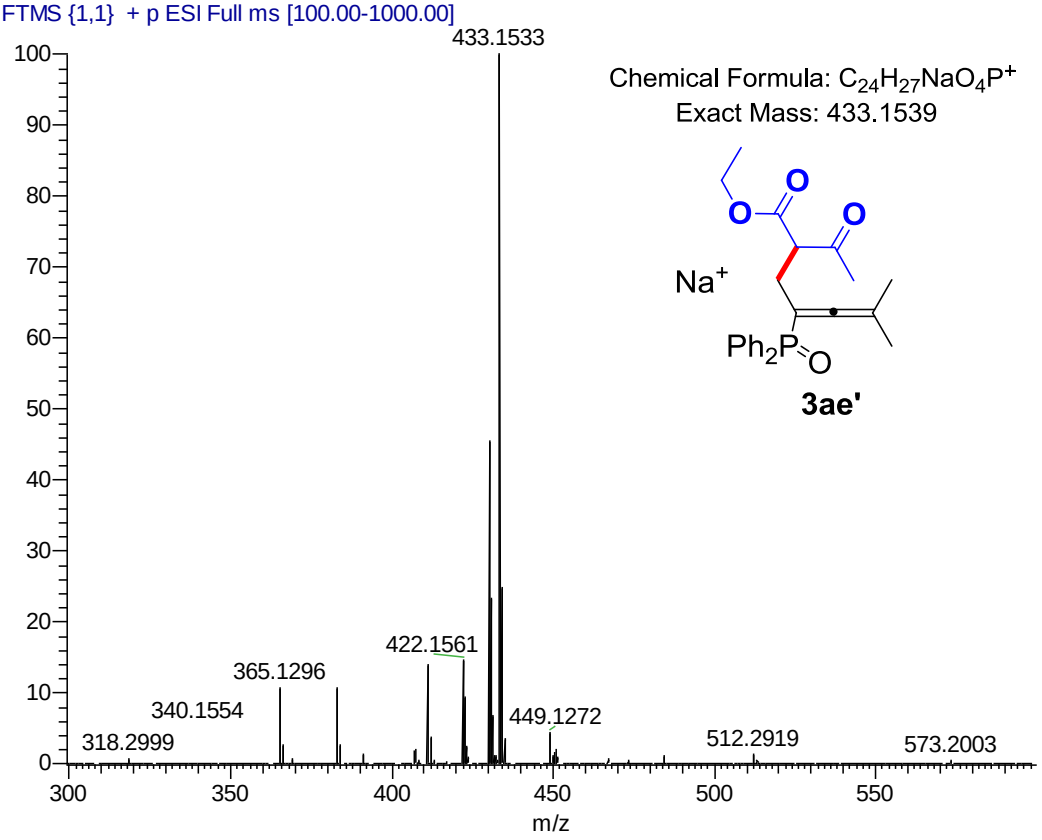


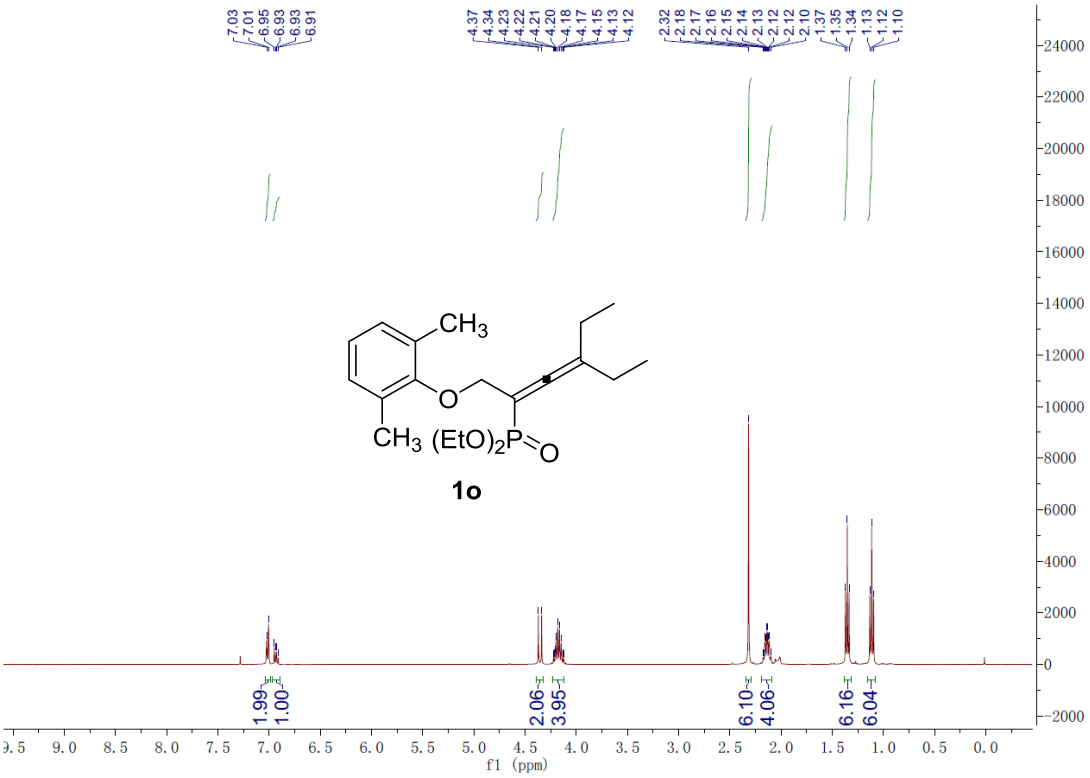

7.67 7.66 7.65 7.65 7.65 7.64 7.63 7.62 7.62 7.61 7.60 7.46 7.45 7.44 7.43 7.43 7.42 7.41 7.40 7.39 7.39 7.38 7.37
4.12 4.11 4.09 4.08 4.07 4.06 4.05 4.04 4.03 3.75 3.74 3.72
2.77 2.76 2.75 2.74 2.72 2.18
1.34 1.32 1.32 1.31 1.19 1.17 1.15
O
O
O
Ph2P
O
3ae'
4.15 6.24 2.09 0.95 2.42 3.00 6.00 2.96
f1 (ppm)

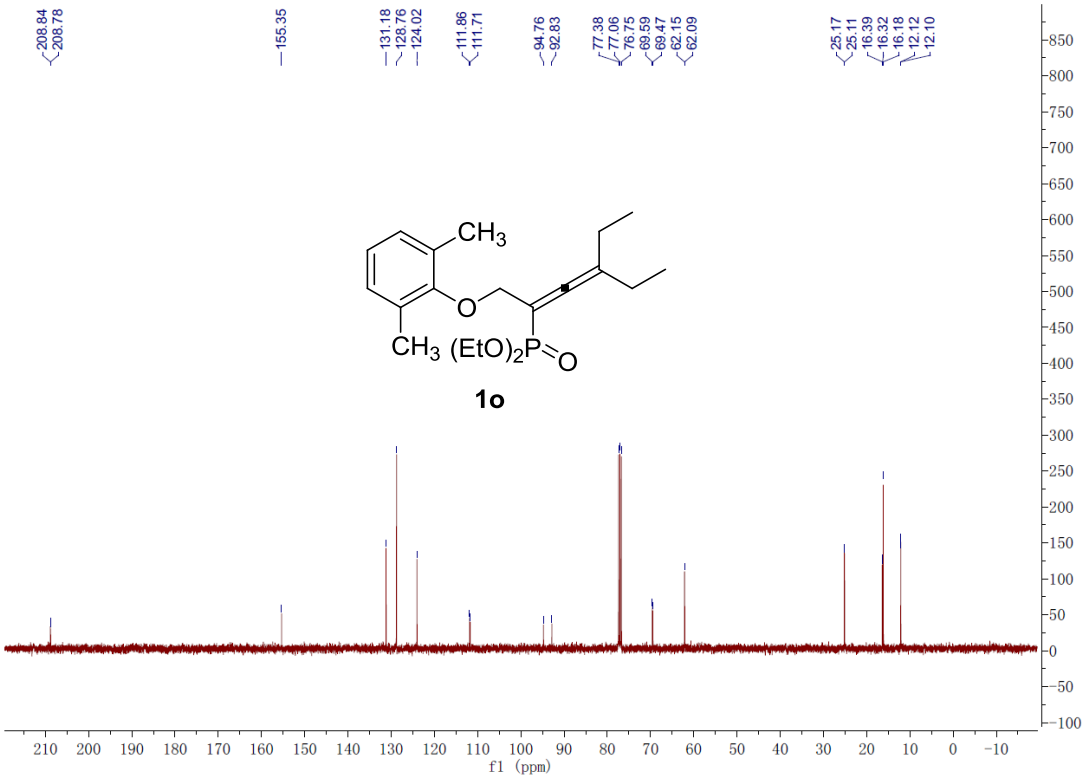

207.07 207.01 202.06
168.68
132.30 132.25 131.80 131.77 131.52 131.48 131.42 131.38 131.26 131.21 128.35 128.33 128.23 128.21
100.60 100.47 94.65 93.62
77.53 77.21 76.89
61.47 58.13 58.07
29.31 26.46 26.36 19.06 19.00 18.95 14.02
O
O
O
Ph2P
O
3ae'
f1 (ppm)

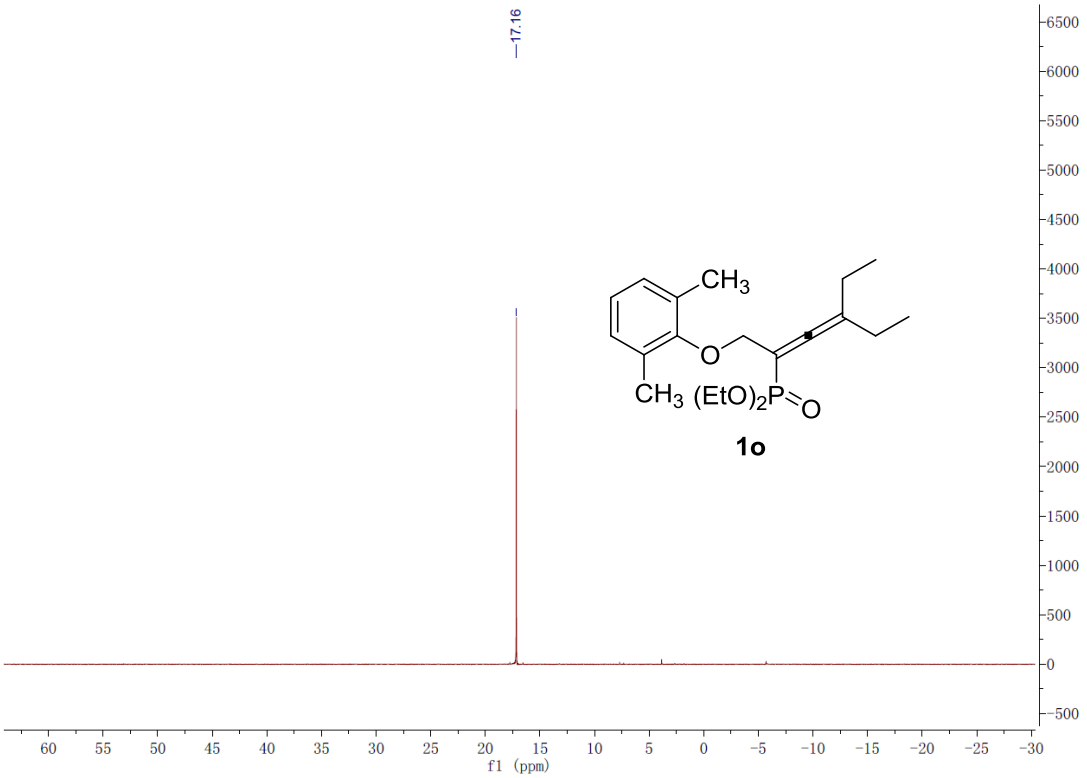



20171228-9 #13 RT: 0.21 AV: 1 NL: 7.21E6
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]




7.03
7.01
6.95
6.93
6.93
6.91
4.37
4.34
4.23
4.22
4.21
4.20
4.18
4.17
4.15
4.13
4.12
2.32
2.18
2.17
2.16
2.15
2.14
2.13
2.12
2.12
2.10
1.37
1.35
1.34
1.13
1.12
1.10
CH3
O
CH3 (EtO)2P=O
1o
1.99
1.00
2.06
3.95
6.10
4.06
6.16
6.04
f1 (ppm)

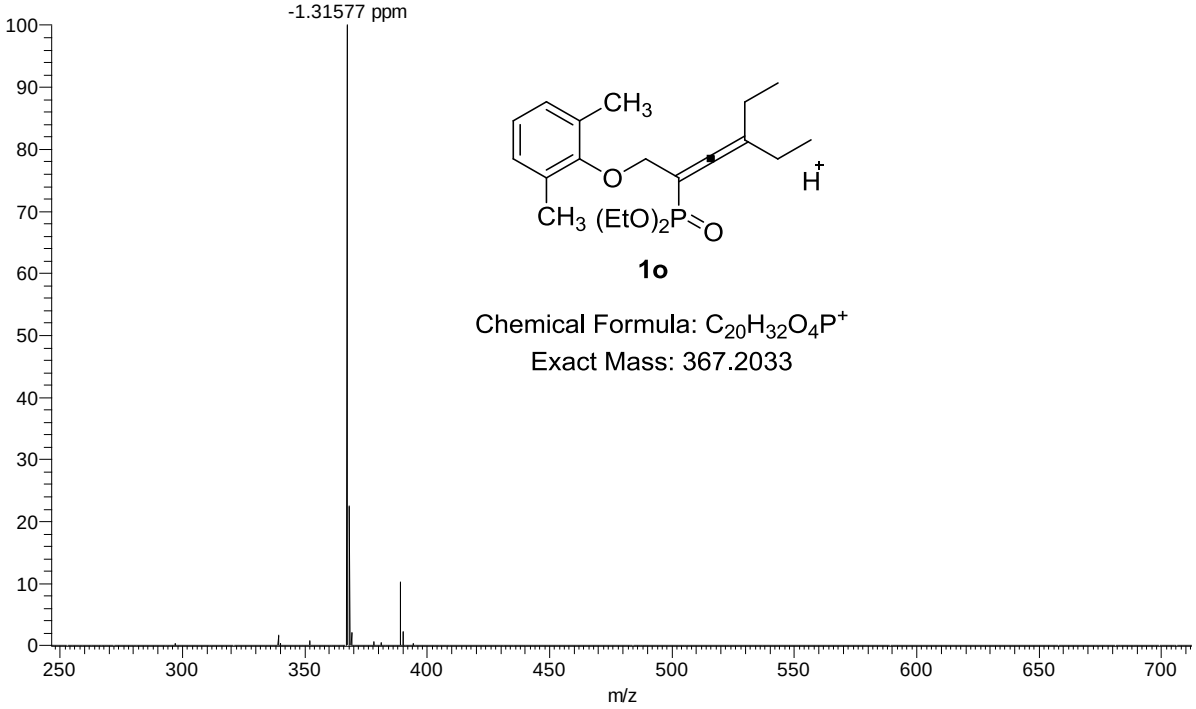

208.84
208.78
155.35
131.18
128.76
124.02
111.86
111.71
94.76
92.83
77.38
77.06
76.75
69.59
69.47
62.15
62.09
25.17
25.11
16.39
16.32
16.18
12.12
12.10
CH3
O
CH3 (EtO)2P=O
1o
f1 (ppm)




**1o**

NJNY-20180817-1 #47 RT: 0.59 AV: 1 NL: 2.59E7
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

367.20279
z=1
$C_{20}H_{32}O_4P$ = 367.20327
-1.31577 ppm

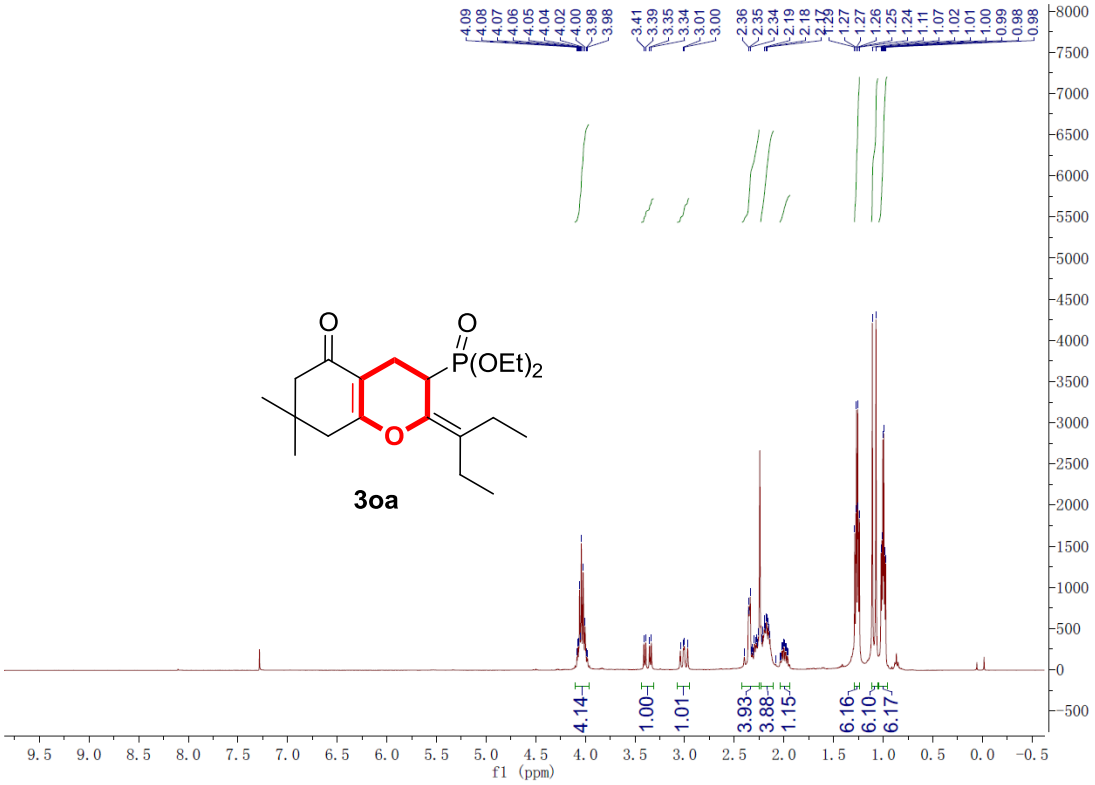


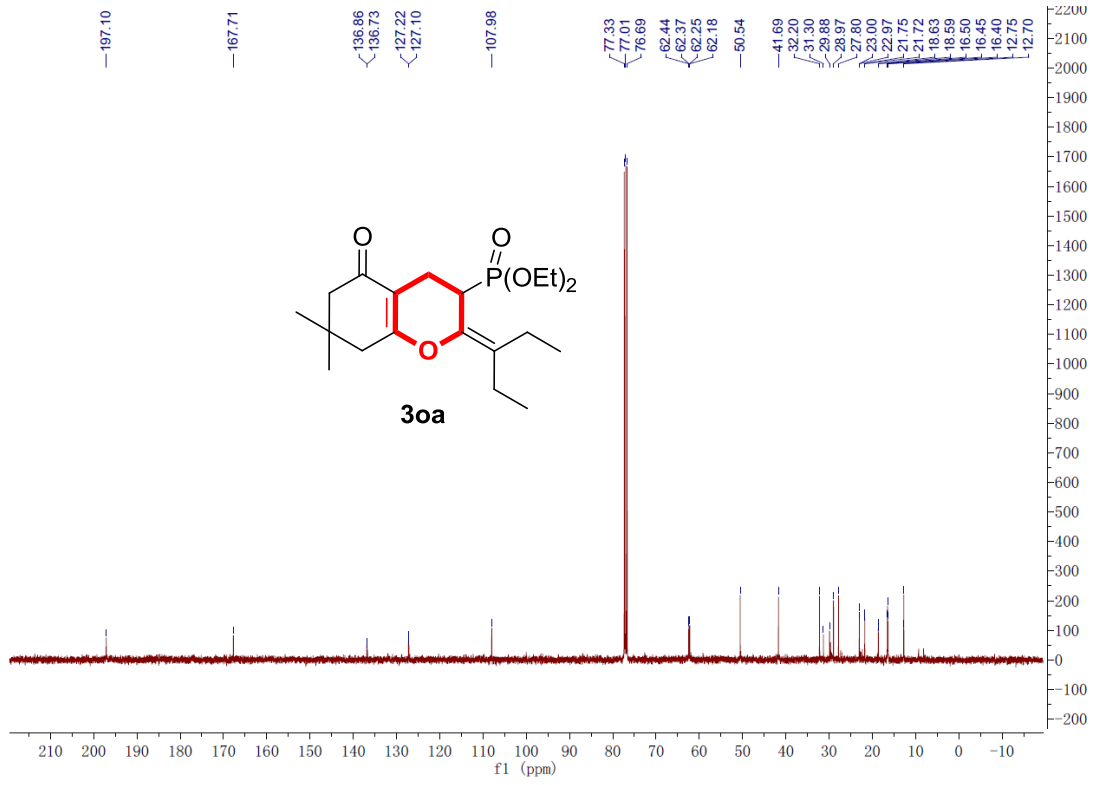


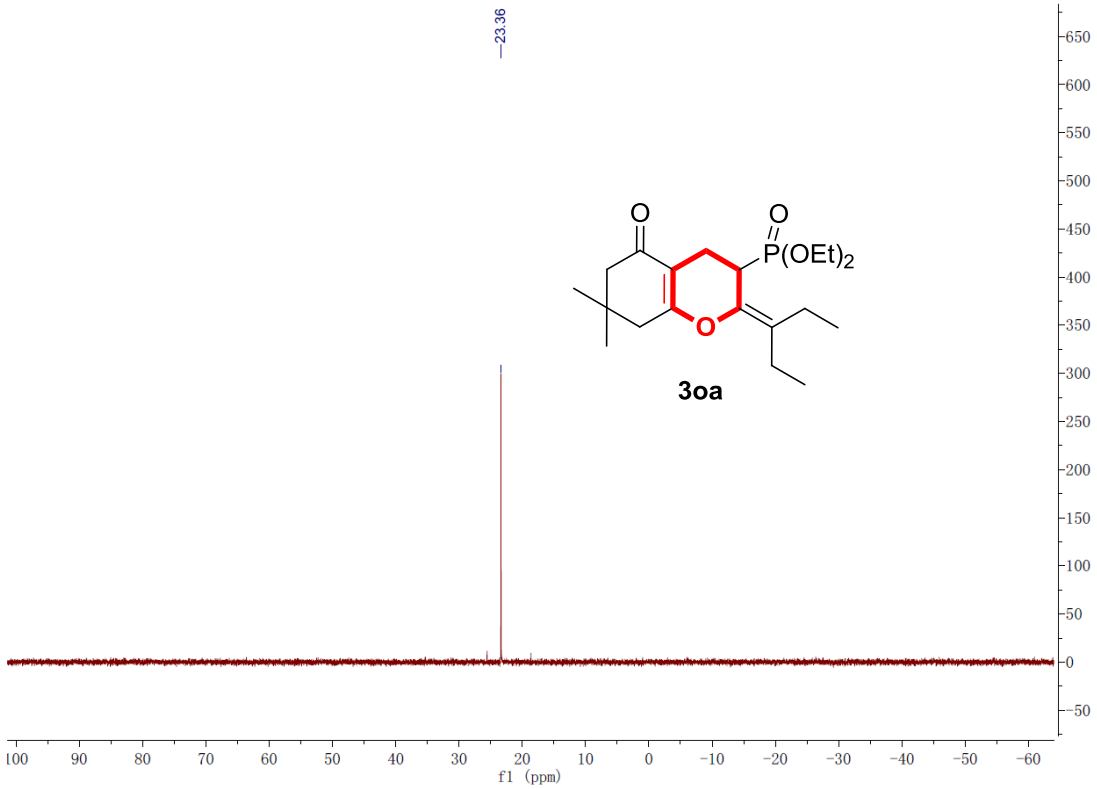


**1o**

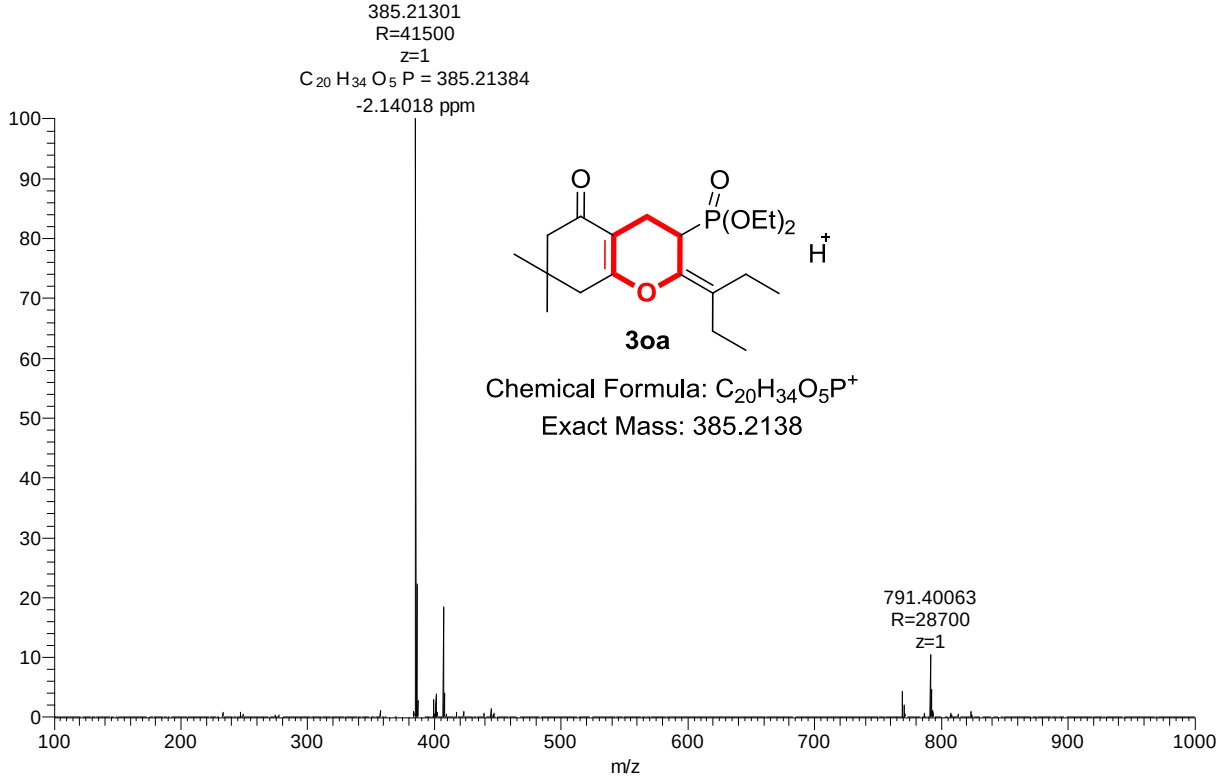
Chemical Formula: $C_{20}H_{32}O_4P^+$
Exact Mass: 367.2033

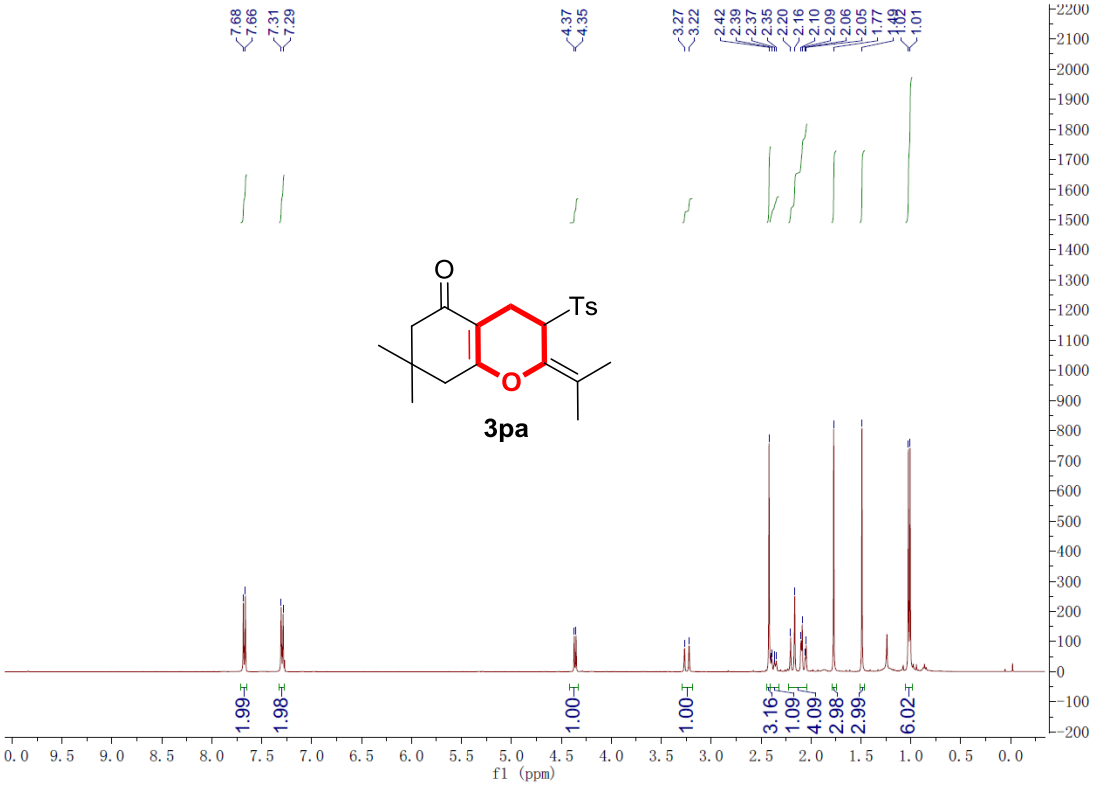

4.09
4.08
4.07
4.06
4.05
4.04
4.02
4.00
3.98
3.98
3.41
3.39
3.35
3.34
3.01
3.00
2.36
2.35
2.34
2.19
2.18
2.17
1.29
1.27
1.27
1.26
1.25
1.24
1.11
1.07
1.02
1.01
1.00
0.99
0.98
0.98
O
O
P(OEt)2
O
3oa
4.14
1.00
1.01
3.93
3.88
1.15
6.16
6.10
6.17
f1 (ppm)

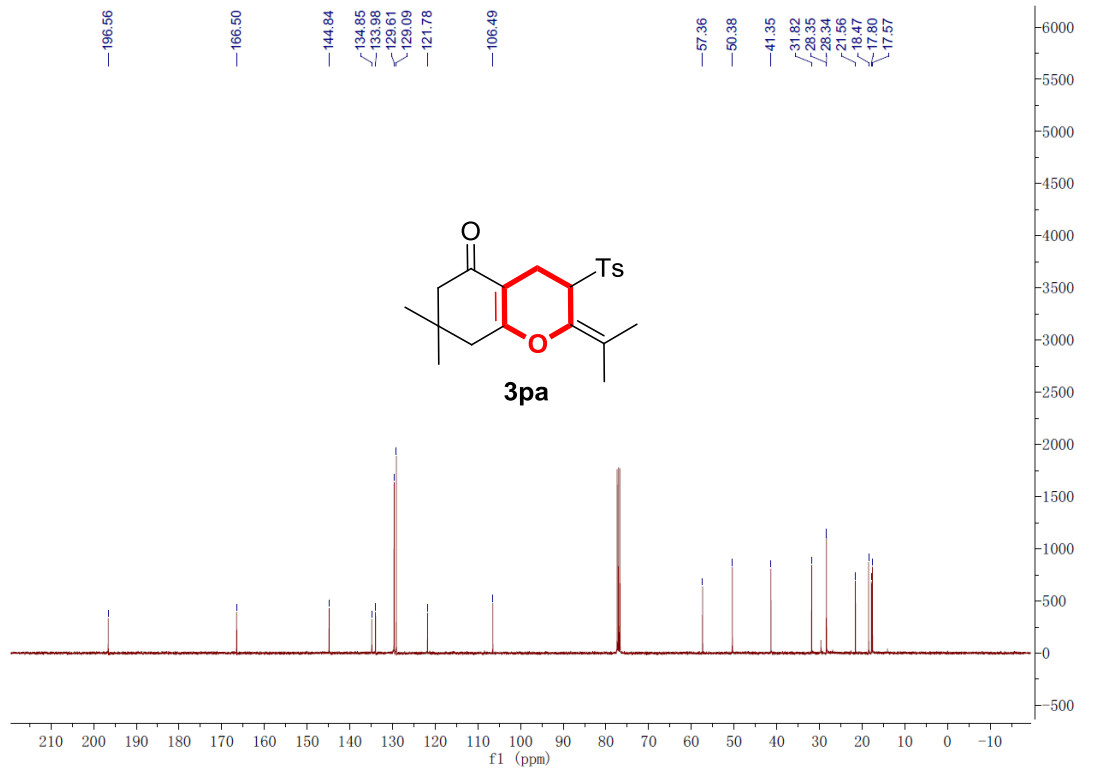

197.10
167.71
136.86
136.73
127.22
127.10
107.98
77.33
77.01
76.69
62.44
62.37
62.25
62.18
50.54
41.69
32.20
31.30
29.88
28.97
27.80
23.00
22.97
21.75
21.72
18.63
18.59
16.50
16.45
16.40
12.75
12.70
O
O
P(OEt)2
O
3oa
f1 (ppm)

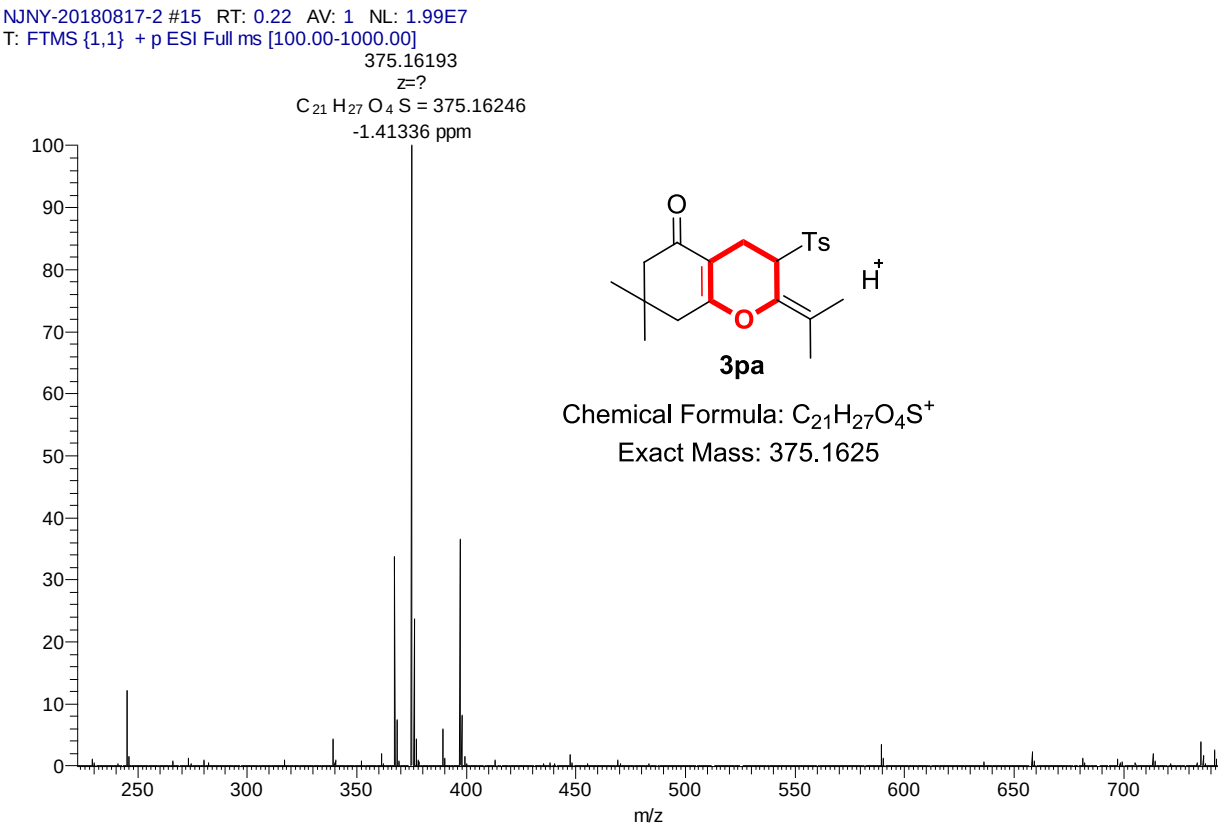



NJNY-20180812-1 #63 RT: 0.88 AV: 1 NL: 1.32E7
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]




7.68
7.66
7.31
7.29
4.37
4.35
3.27
3.22
2.42
2.39
2.37
2.35
2.20
2.16
2.10
2.09
2.06
2.05
1.77
1.01
O
Ts
O
3pa
1.99
1.98
1.00
1.00
3.16
1.09
4.09
2.98
2.99
6.02
f1 (ppm)


196.56
166.50
144.84
134.85
133.98
129.61
129.09
121.78
106.49
57.36
50.38
41.35
31.82
28.35
28.34
21.56
18.47
17.80
17.57
O
Ts
O
3pa
f1 (ppm)


NJNY-20180817-2 #15 RT: 0.22 AV: 1 NL: 1.99E7
T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]
375.16193
z=?
C 21 H 27 O 4 S = 375.16246
-1.41336 ppm
100
90
80
70
60
50
40
30
20
10
0
250
300
350
400
450
500
550
600
650
700
m/z
O
Ts
H+
O
3pa
Chemical Formula: C21H27O4S+
Exact Mass: 375.1625